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THE ADHESION OF THIN METALLIC FILMS

by

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A Thesis

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in the Faculty of Science

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ABSTRACT

A method of measuring the adhesion of thin metallic films deposited on the surface of various materials is studied. The mechanism of this method is examined, both experimentally and theoretically, and it is found that an absolute value of adhesion can be obtained.

Using this method, the adhesion of metal films deposited by vacuum techniques on glass is investigated and it is found that the adhesion depends upon a number of factors, such as the affinity of the metal for oxygen and the structure of the metal film. The effect on the adhesion of the nature and pressure of the residual gas is examined as well as the film structure. The adhesion of metal films to crystal faces and the surfaces of plastics is also investigated.

CHAPTER 1

THE ADHESION OF THIN FILMS

1. Introduction

The uses of a thin film of material, deposited by vacuum technique, on a surface have grown enormously over the last twenty years both in industry and in research. The commercial uses of these thin films for front surface mirrors, metallized plastics, lens blooming, and conducting glass windows, are well established. In research, interference filters, printed circuits and infra-red detection are a few of the many topics which successfully employ these thin films. Needless to say, this increasing use has been attended by much work on the physical nature and properties of thin films. However, one of their main properties, the adhesion to the surface on which they are deposited, appears to have been neglected. In practice, problems of adhesion have been treated in an empirical manner based on experience and this 'folk-lore' has been accepted without question.

Aron[1] states that the adhesion of metallic films to lead glass is only moderate, whereas it improves on

borosilicate glass and is better still on celluloid, fibres, gelatine and bakelite. Williams and Backus[2] have shown that those metals which readily form oxides, such as chromium and aluminium, adhered strongly to glass, while the noble metals, gold and silver, did not. It is also known from general experience that dielectric films on glass and metal films on metals have a high adhesion. On the other hand, the adhesion of metal films to plasticized plastics is usually poor and, though the metals which readily form oxides again tend to have a greater adhesion, the adhesion is rarely comparable to that reached on glass or metal.

2. Theories of Adhesion

In this discussion we consider the adhesion between two solid phases which may be defined as the strength of binding between the two phases. The adhesion will depend on the type of binding at the interface which, in turn, will depend on the nature of the film and the substrate. The types of bond which could promote adhesion between two phases are van der Waals' forces, electrical forces, and chemical bonds. Whether a substrate is amorphous or crystalline, the structure of the surface is different from that of the bulk material. In the bulk material the atoms

are bound on all sides but at the surface the atoms do not have the full co-ordination and therefore the surface exhibits a strong attractive force.

The structure of a metal film deposited on a surface is fundamentally related to the adhesive forces acting between the condensing metal atoms and the surface. If the adhesive forces between the condensing atoms and the surface are high, then an atom in contact with the surface will have a lower energy than one in contact only with atoms of its own kind and not in direct contact with the surface and a monolayer of atoms will be formed. As the thickness of the film increases, this monolayer will tend to build up as a continuous structure. However, if the atoms have sufficient mobility to reach the positions of minimum potential energy, the surface will have a strong influence on the arrangement of the first layer of the film. If the formation of a monolayer is regarded as adding atom to atom, it would be possible for these deposit atoms to take up the same positions as would atoms belonging to the same substance as the substrate. Thus the monolayer may be homogeneously deformed to fit the surface and van der Merwe[3] suggested that this monolayer would be a suitable foundation for the deposition of similarly oriented successive layers and an adherent oriented overgrowth would be built up.

On the other hand, if the adhesive forces are weak, the condensing atoms will have a strong attraction for one another and will tend to move over the surface to form a small number of nucleating centres from which the film will build up with an aggregated structure.

Appleyard[4] has suggested as a criterion for the film structure that the metal would form a continuous structure if the latent heat of evaporation of the metal atom from the substrate surface (L) was greater than the latent heat of evaporation of the metal atom from a surface of the metal itself (L_m). However, if $L < L_m$, then the metal would form an aggregated structure. This implies that the film structure will be aggregated whenever the cohesive energy of the film material is greater than the adhesive energy. The latent heats of evaporation of metals from various surfaces are not readily available; however, Levinstein[5] has shown that the film structure can be correlated to the melting point of the metal from which it is deposited. It was shown that films formed from high melting point metals consisted of microcrystals with no specific orientation, whereas films formed from low melting point metals had a preferentially orientated structure of large crystals.

Rhodin[6], studying the degree and type of orientation present in thin aluminium films formed on ionic substrates, has examined the relationship between the adhesive energy and the orientation. The adhesive energy was first estimated experimentally by considering a beam of metal vapour directed at a heated substrate. For a given vapour pressure there was a critical substrate temperature below which condensation occurred but above which condensation did not occur and any condensed metal atoms were re-evaporated. The relationship between the vapour pressure and the corresponding critical substrate temperature could be expressed as

$$p = c.e^{-\frac{A}{RT}}$$

where p is the pressure of the metal vapour, c is a constant insensitive to temperature, T is the absolute temperature of the substrate, and A is an energy term characteristic of the film and substrate. By varying the substrate temperature and finding the corresponding vapour pressure for condensation, a value of A could be obtained for each film-substrate pair.

The term A was expressed as the sum of two components

$$A = E + \Delta$$

where E is the adhesive energy between the first layer of the film and the substrate and Δ is the cohesive energy in this first layer. By estimating Δ, Rhodin found the adhesive energy, E, for each film-substrate pair.

In an attempt to explain the adhesive energy found experimentally for each film-substrate pair, Rhodin considered the forces at the interface to be similar to adsorption forces exerted on a gas by an adsorbing medium. The relative magnitude and non-specific nature of the adhesion suggested van der Waals' adsorption forces.

The adsorption energy between an atom, i, and an adsorbing medium of ions, k, which results from van der Waals' adsorption forces, is given by London[7] as

$$E = \frac{N\pi}{4} \cdot \frac{a_i a_k}{d^3} \cdot \frac{J_i J_k}{J_i + J_k}$$

where a_i and a_k are the polarizabilities of the atom and the substrate ion respectively, J_i and J_k are the characteristic energies of the atom and the ion respectively, N is the number of ions per unit area of the substrate, and d is the distance of the atom from the surface of the substrate.

Rhodin based his theoretical calculation of adhesive energy on this expression and, though a number of

approximations were made, it was shown that there was a good agreement between these theoretical values and the experimental work. It was also shown that the degree of orientation in an aluminium film with respect to the substrate could be correlated to the adhesive energy characteristic of the substrate.

A contribution from Russia by Deryagin and others[8] claims a new electrical theory for the solution of problems of adhesion. They suppose that when two bodies, either metal or non-conducting, are brought into contact an electric double layer would be set up at the boundary so that positive charges would be distributed over one side of the boundary and negative charges over the other side. Thus a certain potential difference would be set up across the boundary which may be a fraction of a volt or several volts, depending on the nature of the two phases and the transfer of charge between them.

Their experimental method of measuring the electrical forces of adhesion is not practicable in the case of vacuum deposited films as the film has to be stripped from the substrate without fracture. However, it is interesting to consider the suggested theory behind the method.

When the adhering film can be stripped quickly from the surface of the substrate so that separation occurs at the boundary, the charges of any double layer would be separated in the process. As the separation proceeds the potential difference between the film and the surface would increase in proportion to the distance, h, between them, the potential difference being limited only by the onset of an electrical discharge in the gap. The type of discharge would depend on the surrounding gas pressure, p. Provided that the gas pressure was not too low, disruptive discharge would occur.

Assuming Paschen's law of gas discharge, the discharge potential, V, and the separation at discharge, h_d, could be calculated if the charge density per unit area, σ, for the electric double layer was known. In this way, the amount of work, A, involved in separating the film from the substrate against electrical attraction could be determined from the expression:

$$A = 2\pi\sigma^2 h_d = \frac{\sigma V}{2}$$

It was found to be difficult to deduce the values for σ and equally difficult to measure them. Therefore Deryagin used Paschen's law to predict the way in which the discharge gap, and therefore the work per unit area,

varied with the nature and pressure of the surrounding gas. The values of the ionising potentials, V, were obtained by experiment on a discharge tube at various pressures. Selection of a suitable value for σ gave values of A which were in good agreement with the values found by actually stripping the film from the substrate.

There have been some objections to this new theory, principally why the breakdown takes place at the double layer and not a cohesive break at some weak point in the film material, especially when the double layer has, in many cases, the strength of a strong chemical bond. Deryagin explained this by considering two different mechanisms in removing the film. If the breakdown occurred simultaneously over the whole contact area, the applied stress would be the significant factor and the break would arise at the weakest area under the given load. On the other hand, if the break occurred by peeling, the significant factor would be the amount of work involved in the process and this may be considerably more than the minimum possible. Thus, the principle of least resistance would no longer hold good.

The idea of electrical phenomena playing a major role in adhesion has been considered by other workers, for example, Skinner, Savage and Rutzler[9] in dealing with

metal-polymer adhesion. Briefly, the mechanism suggested here was the migration of the electron gas in the metal into the conduction bands of the polymer. The potential barrier at the contact of the two phases would be considerably reduced and a large number of electrons would be able to migrate even at room temperature. This electron cloud would remain very close to the interface owing to the positive charge now assumed by the metal.

This concept of electrical adhesion forces has been used to explain the results of work on the properties of thin unsupported films. Meissner[10] found the adhesion forces in these unsupported films increased rapidly with decreasing thickness below a critical thickness of 0.25μ. A film of any substance which had a thickness less than 0.25μ adhered on contact with a metallic surface and after contact had been made on one side of the film, no adhesion was obtained to a second metal surface brought up to the other side of the film. Skinner et al.[9] suggested that contact with the first metal surface would establish an atmosphere of electrons in the first portions of the film which came in contact thus drawing up the remainder of the film to the metal surface. This would occur if the thickness of the film was not so great as to require forces greater than those provided by the electron atmosphere.

The atmosphere would be established in the whole film giving complete adherence. Any second metal surface approaching from the other side would encounter a space charge filled adhesive film and would suffer a mild electrostatic repulsion. Thus there would be no adhesion.

The author considers that there may be other explanations for the large adhesion forces observed in these unsupported films at small thicknesses. A metal surface, no matter how smooth, will have small scale asperities[11]. When this surface is brought into contact with a thin unsupported film one of two things can happen. If the film remains rigid then contact between the film and the metal surface will occur at the high spots and the adhesion will be weak. On the other hand, if the unsupported film is flexible, it will be deformed to contour the metal surface and the ensuing strong adhesion will be due to surface tension. This change between a rigid and a flexible film could occur at this critical thickness of 0.25μ and, of course, as the film becomes thinner so its ability to contour the surface will increase and the adhesion forces will become stronger. It follows that once an unsupported film is bound to a metal surface by surface tension, it cannot be deformed to contour a second metal surface brought up on the opposite side of the film and, hence, there will be little adhesion to this metal

surface since once again contact will occur only at the high spots.

Finally, there is the chemical picture of adhesion. Here it is assumed that the adhesion of the two materials is primarily a formation of new chemical bonds. Weyl[12] uses this idea in his classification of the forces of adhesion acting on a glass or crystal surface. The forces can be divided into three classes. Firstly, the adhesion due to the continuation of the glass or crystal structure with other building units. Here the forces endeavour to continue the surface structure. If the same building units are not available, the structure may be continued by other compatible units. Secondly, the continuation of the glass or crystal structure by an intermediate oxide layer. The third and final class is based on a different principle. Where no oxide film is formed, an ionic substance may adhere to a metal by 'mirror forces'. Here Weyl bases his arguments on the classical polarization theory of Fajans[13]. The structure of a metal is such that it is a highly polarizable system. On the approach of a checkered positive and negative surface a corresponding checkered pattern of the opposite sign is induced in the metal. The metal, being neutral in itself

but highly polarizable, cannot exert strong forces of its own but it will mirror the forces emanating from the ionic surface. If these forces are strong then the adhesion will be strong.

Bateson[14] has used the second of the above classes together with Weyl's conception of the physical nature of a glass surface[15] in an attempt to explain the adhesion of metal films to glass.

The basic principle governing the structure of glass is that the Si^{4+} ion is always surrounded by precisely four oxygen ions. Each oxygen ion is on the average shared by two silicon ions. Weyl suggested that when a piece of glass was fractured, creating two fresh surfaces, an equal number of units, either with an unco-ordinated oxygen ion or minus an oxygen ion, would remain on each side of the fracture. These units would make up a neutral layer of structural units

$[Si^{4+}(\frac{1}{2}O^{2-})_3\ O^{2-}]^-$	$[Si^{4+}(\frac{1}{2}O^{2-})_3]^+$
E unit	D unit
Excess of oxygen	Deficient in oxygen

In the D unit, the silicon ion would have incomplete co-ordination and an excess of positive charge. Consequently,

the unit would attract and combine with constituents of the atmosphere

$$[Si^{4+}(\tfrac{1}{2}O^{2-})_3]^+ + H_2O \rightarrow [Si^{4+}(\tfrac{1}{2}O^{2-})_3\ OH^-]^o + H^+$$

There would now be a neutral layer of OH groups on the surface of the glass. Bateson proposed that the adhesion of a metallic film to the glass surface was accomplished by a chemical reaction with this layer. This exposed OH layer could also retain a weakly bound layer of water vapour or fatty acid but cleaning by a gas discharge in vacuo would remove this layer though not the OH groups. Thus, under ideal conditions the glass surface would be in a highly 'reactive' state at the instant of depositing the metal film and the metal vapour impinging on the surface would react chemically with the OH groups displacing hydrogen.

According to this theory, metals which readily form oxides should adhere firmly to the glass surface. This has been shown previously to be true from practical knowledge. Bateson also suggested that the adhesion between a metal and a glass substrate would be greater for metals with cations of a low ionic radius and also a co-ordination number similar to that of the silicon ion.

Evidence for the presence of an intermediate

oxide layer has been given by Beeching[16] and more fully by Stahl[17]. The latter has examined by electron diffraction the structure of thin films of a number of metals deposited on outgassed metal, glass and mica surfaces. The metal oxides were shown to be present for all metals up to a film thickness of 500-1000A. Only for Be, Al, Mo and Ni did the metal space lattice become evident at film thicknesses greater than 1000A. However, these thickness values seem to be very high and should be treated with care.

The formation of this intermediate layer of metal oxide may not be due to a chemical reaction with oxygen bound to the substrate. For example, Stahl suggests that the residual adsorbed oxygen in the system would be released by a gettering action of the metallic vapour so that at the beginning of the evaporation the metal atoms would combine with the residual oxygen surrounding the source forming the metallic oxide. As the evaporation continues at a constant rate the space would become depleted in oxygen and the metal atoms would reach the substrate unchanged. Thus the deposited film would gradually build up from the oxide to the metallic space lattice. If the evaporation was interrupted oxygen would enter the space around the source and on restarting the evaporation a second oxide layer would be formed.

However, under the conditions employed by Stahl, the oxide formation is more likely to be due to collisions of the residual oxygen molecules with the surface of the slowly forming film. Stahl used a very small source to substrate distance and, even though the gas pressure was relatively high, very few metal atoms would collide with oxygen molecules before reaching the substrate. The slow rate of deposition at these pressures would, however, allow the residual oxygen molecules to react with the film surface as it formed. Thus the metal oxide would be formed until the supply of oxygen became insufficient and the film would then build up as the pure metal.

3. Measurement of Adhesion

There are a number of empirical methods for the measurement of adhesion between a film and the surface on which it is deposited. These methods really stem from the time-honoured 'thumb-nail' test.

Strong[18] was the first to use the 'Scotch Tape' method for testing the adhesion of aluminium films to glass. However, this method, in which the adhesive tape is pressed on to the film and then stripped off, is of little use as a quantitative test. The test is dependent on the adhesion between the tape and the film and, since the film may be

completely or partly removed, or not removed at all by the stripping action of the tape, one can only judge three degrees of adhesion between the film and the substrate. No degree of adhesion could be judged if the adhesion was good.

An instrument to measure the force required for a sharp-edged chisel to strip paint films from a surface has been used by Rolle and Dietrich[19]. This stripping force, F, can be expressed in terms of three components; T, the tear resistance of the film on either side of the chisel, P, the plastic resistance of the film to the pushing action of the chisel, and A, the force of adhesion at the interface. Only A is independent of film thickness. Having measured the force to strip a 4 mm. width of film, the chisel is moved a distance less than 4 mm. to one side of the first strip and the force required to remove a second strip of film is measured. In the second case, only one edge is subject to tearing and, by measuring the second width, T can be eliminated and a value for P + A obtained. If P + A is found for a series of film thicknesses and extrapolated to zero thickness a value for A can be estimated for the film-substrate pair. In this way, values of A have been found for paint films 0.0005 - 0.004" thick on various metal surfaces. In this method of adhesion measurement the sharp-edged chisel digs into the film to lift

it from the surface and the mechanism holds good when the film thickness is greater than the dimensions of the chisel edge, as in the case of the paint films. This mechanism could not hold for thin evaporated films where the dimensions of the chisel edge would be much greater than the film thickness and it would ride over the surface of the film. It is doubtful whether stripping would occur, and, if stripping did occur, the film would not be completely removed unless the adhesion was extremely poor and the film could be removed by the rubbing action of the chisel edge alone. The analysis of the results would certainly not be applicable and the force could not be broken down into its three components.

For a quantitative test it is quite common practice to determine the mar resistance of a film by abrading the surface. Townsley[20] has described an apparatus in which the specimen film is rotated while an abrading head moves backwards and forwards over the film surface. The film is subject to a fixed number of abrasion strokes under the conditions of constant abrading area and pressure and a comparison can be made as to the extent of the surface marring between different specimens. The result is more a measure of hardness than adhesion and, furthermore, errors may be introduced by the burnishing effect of the abrading head. The abrading head may break down the crystallites

in the film and make it more compact thereby increasing the hardness and the adhesion, or a surface layer of oil may be uniformly spread over the surface and act as a lubricant.

The disadvantages of the methods so far described are eliminated in a method employed by Heavens[21] when investigating some of the factors influencing the adhesion of films. The load required on a chromium-steel point in order to remove the film from the substrate was measured. The point had a smooth contour and was drawn across the film at a constant rate. In testing the adhesion of a film increasing loads were applied to the point until the film was removed completely from the substrate. Burnishing was eliminated since the film was removed in one stroke when the critical load was reached and the use of a single point instead of multiple cutting edges, as in Townsley's method, ensured readily reproducible results. Thus the method gives accurate quantitative results especially when the measurement of small differences in adhesion is required. The load applied to the point to remove the film is limited only by the strength of the substrate and therefore high adhesions can be measured.

The methods described have all been empirical giving only a relative measure of the adhesion. This does not mean that there have been no attempts to measure

directly the absolute value of adhesion. However, the measurement of this value is a very difficult task since a uniform force has to be applied normal to the interface between the film and the surface to break the adhesive bonds. The difficulty of ensuring this has been shown in the work of Bowden and Tabor[22] on friction.

Beams and his colleagues[23,24,25] have designed an apparatus in which this uniform force is applied at the interface by centrifugal methods. Thin films were electrodeposited or evaporated on to the peripheries of cylindrical steel rotors which were suspended in high vacuum and spun at high speeds. The films were circumferentially disconnected into small patches to eliminate hoop stresses due to the tensile strength of the film material and, to prevent these patches loosening round the edges and ripping off, the deposits were made slightly thinner at the edges so that this was the last part to fly off. Centrifugal fields of the order of 10^9 times that of gravity have been reached and the speeds attained are limited only by the bursting strength of the rotors. The apparatus to obtain these high speeds is both mechanically and electronically complex. Most of the work described has been with electrodeposited films on contaminated steel rotors where the adhesion has been poor, even so the rotor

speed required to throw off these films has been very high. Unfortunately, only a few adhesion values are given in the literature; for example, a force of 16,400 lb./in^2 was required to remove an electrodeposited chromium film of thickness 0.01" from a contaminated steel rotor. If the film was only 500A thick, then the acceleration of 3×10^{10}g would be required and this considerably exceeds the centrifugal fields of 10^9g obtained by Beams. However, let us consider the same poor adhesion of 16,400 lb./in.^{2} to exist between an evaporated chromium film 500A thick and a glass cylinder 1 cm. radius. By Beams' formula, a speed of 30×10^3 r.p.s. would be required to break the adhesive bonds but the glass cylinder, with a tensile strength of 5×10^8 dynes/cm.^{2},[26] would burst at 3×10^3 r.p.s. Thus the use of rotors made from materials weaker than steel would be restricted to very poorly adherent films deposited to a considerable thickness. It appears that this apparatus is not suitable for a comprehensive study of the adhesion of thin films deposited on a wide variety of materials.

Ultrasonic vibrations have been used by Moses and Witt[27,28] to apply a force normal to the interface between a film and a surface. The film is deposited on the end of a cylinder in which longitudinal vibrations are

induced electrodynamically. The film separates from the surface when the force due to acceleration exceeds the adhesive force at the interface. In the apparatus used by the above workers the vibration requirements limited the cylinder material to dural and magnesium and the adhesion of organic films to these materials was examined and shown to be poor, accelerations of the order of 5×10^5g being required to remove the films. Considering a chromium film 500A thick with an adhesive force of 16,400 lb./in.^{2} binding it to the surface, again it is seen that an acceleration of 10^{13} cm./sec.^{2} or 10^{10}g would be required to separate the film from the surface. This order of acceleration would certainly not be produced electrodynamically or by magnetostriction since both types of transducer work at the low end of the ultrasonic frequency range. However, a quartz crystal generator, which can work at higher frequencies, produces greater accelerations at the surface. Even so, using a 10 Mc/s quartz crystal to produce an acoustic intensity of 10 W/cm.^{2} in air, the acceleration produced would be about 10^{12} cm./sec.^{2},[29] - an order of magnitude lower than required to remove even a poorly adherent film. Again it has been shown that a method of measuring the absolute value of adhesion between a film and a surface has a limited use and is not suitable where strong adhesion bonds are involved.

4. Conclusions

It can be seen from this discussion of the adhesion between a thin film and its substrate that there is still some doubt as to the actual mechanism of adhesion. From the theories quoted the adhesive bonds could be intermolecular, electrical or chemical. It is possible that the adhesion is due to a combination of these different types of bond.

In an experimental investigation of adhesion, the ideal apparatus should give absolute values of adhesion between the film and the surface. In this case, however, it has been shown that the methods available are only suitable for poorly adherent films such as organic films. Therefore, use must be made of a method which will only give comparative measurements of adhesion and the obvious choice is the apparatus described by Heavens. With this apparatus accurate quantitative comparisons can be made for the adhesion between various metal-substrate pairs over a range from poor to very strong adhesion.

Comparison of the results of the experimental investigation with a theoretical estimate of the adhesion should give an indication of the mechanism of adhesion. The adhesion due to van der Waals' forces can be calculated

most easily and there is the advantage that these values can be checked experimentally by the method described by Rhodin.

With this combination of experimental and theoretical methods for studying adhesion, a comprehensive investigation of the adhesion of metal films on a wide variety of substrates can be made.

CHAPTER 2

THE DETERMINATION OF THE ENERGY OF ADHESION

1. Introduction

The method used to determine the adhesive energy of binding between a thin metallic film and a substrate closely follows that described by Rhodin[6].

When a stream of metal atoms impinges on a substrate, condensation will occur only if certain requirements are satisfied; that is, for a given substrate temperature there is a critical vapour pressure of the stream of metal atoms above which condensation will occur but below which any condensed metal will re-evaporate. The relationship between the pressure and the corresponding substrate temperature is given by

$$p = c.e^{-\frac{A}{RT}}$$

where p is the pressure of the metal vapour stream, T is the absolute temperature of the substrate, c is a constant insensitive to temperature, and A is an energy term characteristic of the film and substrate. This relationship may also be written in the form

$$-\log_{10}p = \frac{A}{2.3R}\cdot\frac{1}{T} - \log_{10}c$$

This is the equation of a straight line from which values of c can be extrapolated from the intercept on the pressure axis and values of A obtained from the slope of the line.

A may be interpreted as being the heat of condensation of the first layer of metal atoms on the substrate and can be divided further into the adhesive energy between the metal and the substrate (E) and the cohesive energy in the first layer of metal atoms (Δ), that is

$$A = E + \Delta$$

To measure A experimentally for a metal-substrate pair, the substrate temperature is varied and for each substrate temperature the corresponding minimum vapour pressure for condensation is found. In practice, the vapour pressure of the stream of metal atoms is obtained from the metal source temperature using the values for the variation of vapour pressure with temperature for the metal concerned[30].

2. Apparatus

The apparatus used in this investigation is shown in Figure 2.1. The metal to be deposited was placed in a microcrucible, M, made of either tantalum or molybdenum, and heated by electron bombardment. The metal vapour stream from the crucible was passed through a series of apertures, A, and was directed on to a substrate, S (shown in Figure 2.1 as a glass slide), which was heated from the opposite side by a massive copper block, C. This block contained a heating element, H, which was controlled directly by a Variac. The substrate temperature was measured by a thermocouple in intimate contact with the exposed surface. In the case of a glass substrate, a silver-platinum thermocouple was fired on to the surface but with crystal substrates, a chromel-alumel thermocouple was pressed on to the surface. The formation of the metal film was detected by a sudden drop in resistance between two contacts also in intimate contact with the surface and, for both glass and crystal substrates, silver contacts were fired on to the surface for this purpose. Figures 2, 2(a) and 2.2(b) show a glass and a crystalline substrate with the positions of the thermocouple and its contacts, the resistance probes, and the area covered by the condensed metal film. Connections to the substrate were made by

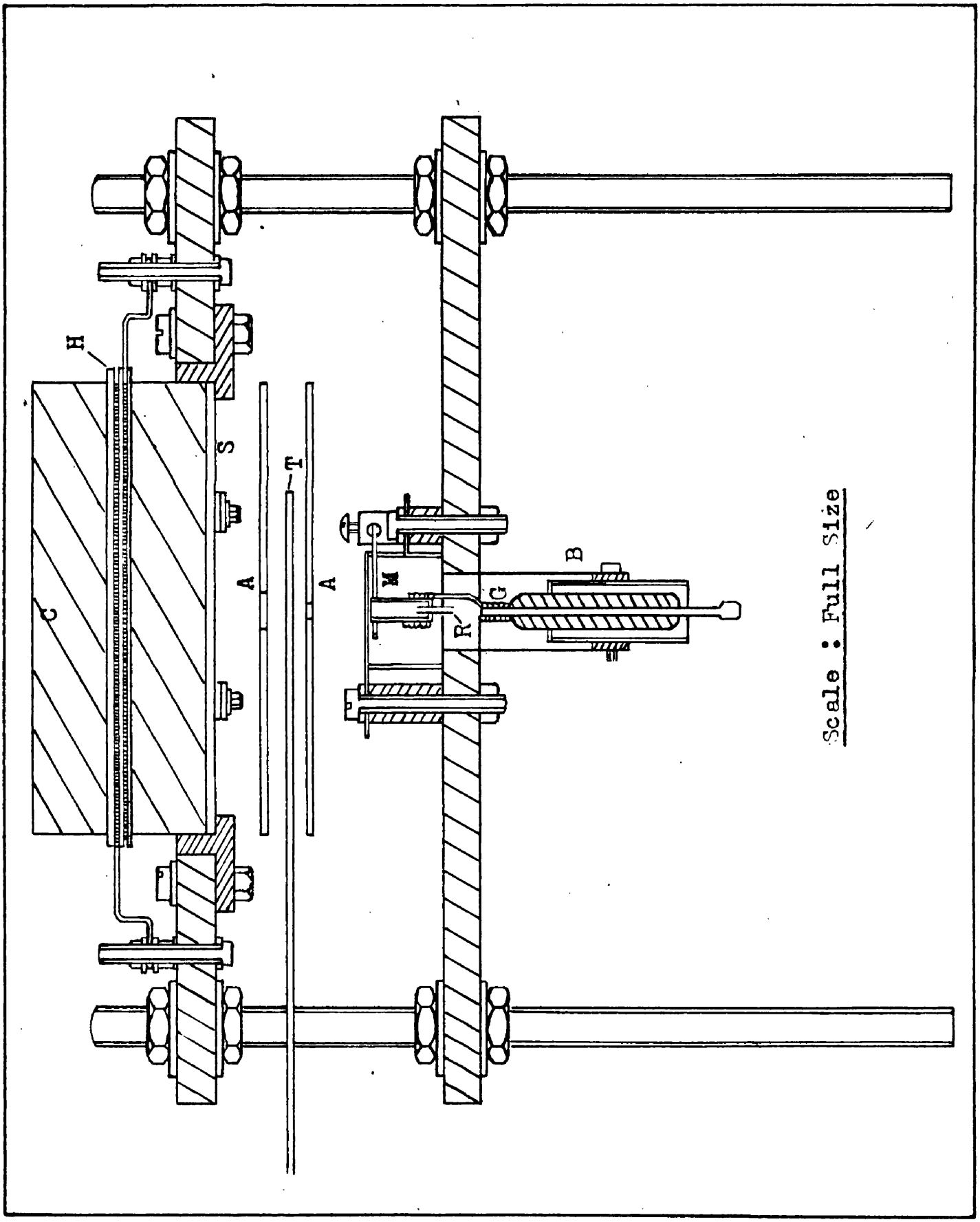


Figure 2.1. Sectional view of apparatus for the determination of adhesive energy.

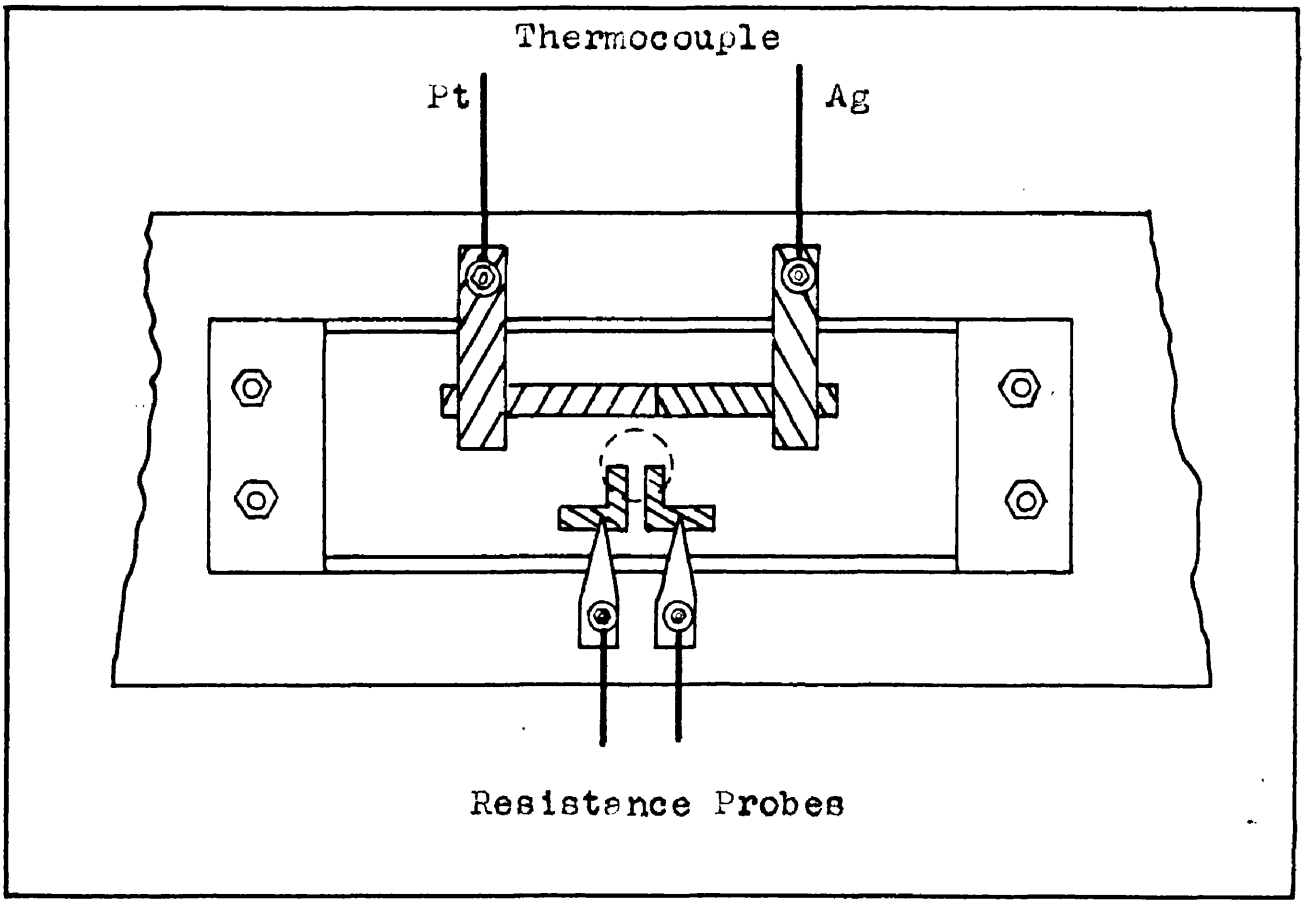


Figure 2.2a. Diagram of contacts to a glass substrate.

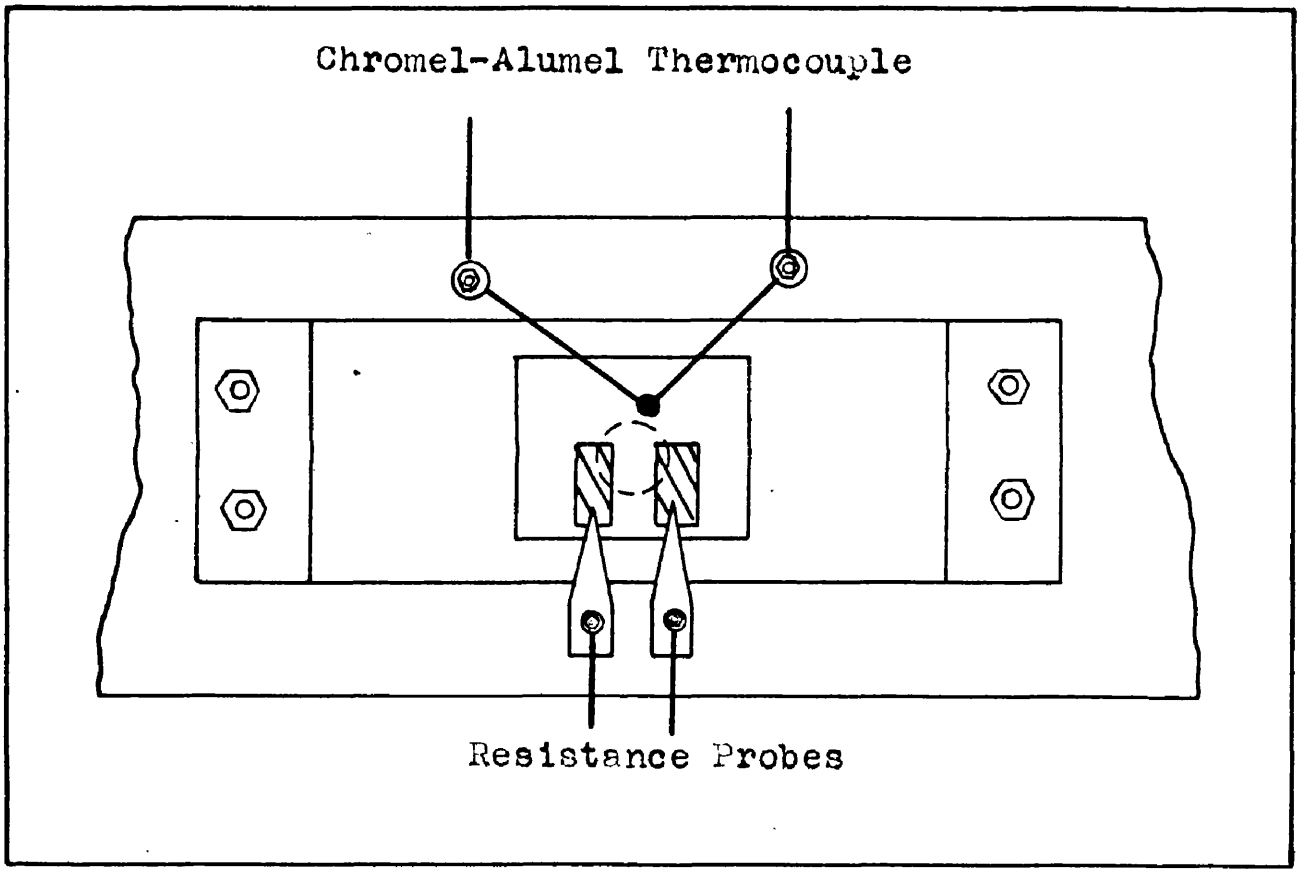


Figure 2.2b. Diagram of contacts to a crystal substrate.

phosphor bronze pressure contacts, though for the Ag-Pt thermocouple these contacts were covered by silver and platinum foil.

The heating of the microcrucible by electron bombardment was carried out by the system shown in Figure 2.3. The crucible, with an inside diameter of approximately 0.35 cm., was mounted at the centre of a tungsten filament. This filament, of 0.005" wire, when heated to white heat, emitted electrons which were accelerated by a positive potential of 1 - 2 KV towards the crucible. The system was surrounded by a tantalum shield to prevent heat losses and the metal vapour was emitted through an orifice of approximately 1 mm. diameter in a tantalum lid which completely enclosed the whole system. The microcrucible was mounted by molybdenum wire to a glass-metal seal (G in Figure 2.1), which, in turn, was soldered to a copper cylinder (B in Fig. 2.1) to enable it to be clamped. This mounting considerably reduced heat conduction. With independent control of the filament voltage and the accelerating potential, the source temperature could be accurately controlled to temperatures up to 1500°C. These high temperatures were measured by a thermocouple actually in the crucible, the 'couple being led in by a silica tube (R in Figure 2.1) through the

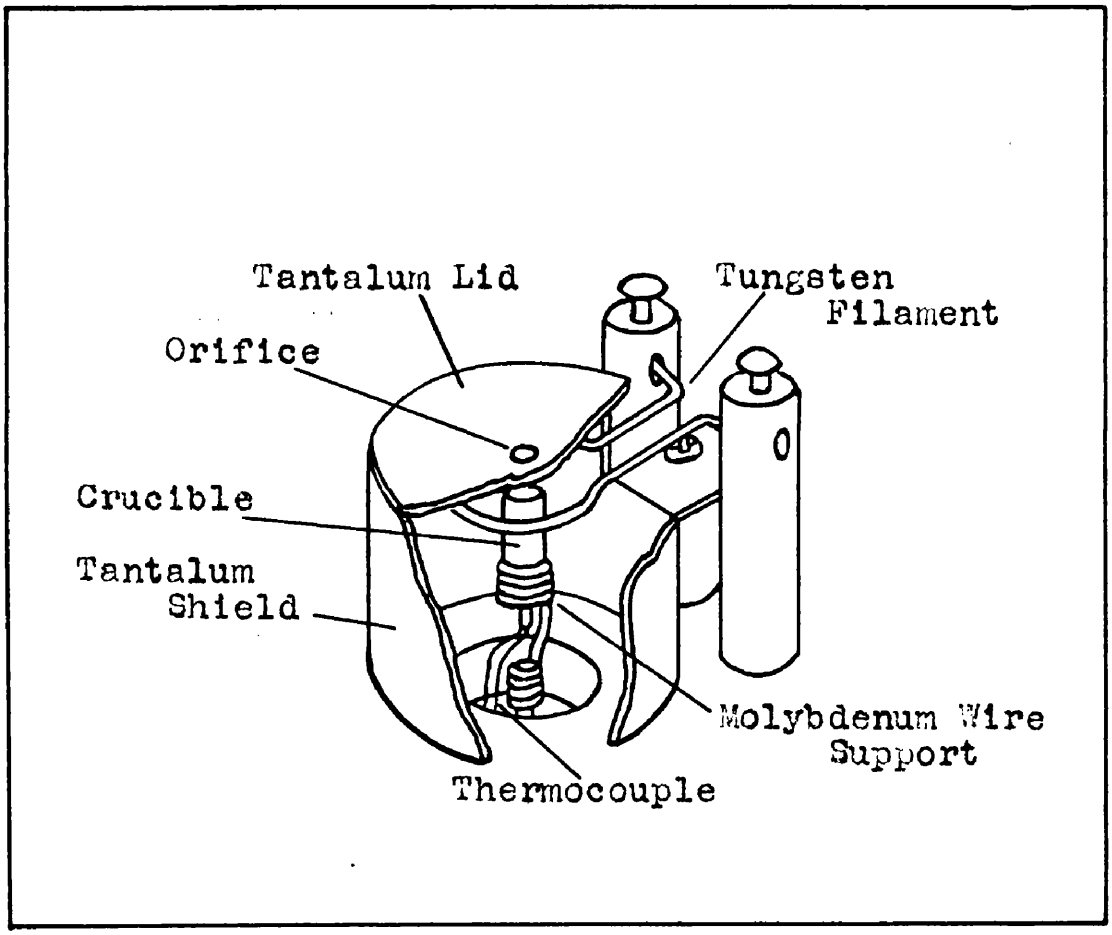


Figure 2.3. Diagram of the electronic heater.

bottom of the crucible. The thermocouple used was chromel-alumel, though platinum-platinum/rhodium was tried but was found to burn out due to crystallisation of the platinum. Cambridge 'Spot' galvanometers were used to record the thermocouple readings. Where chromel-alumel was used, the scale was calibrated from the standard temperature-E.M.F. tables. However, in the case of the silver-platinum 'fired' thermocouple, it was doubted whether the calibration would be the same as an Ag-Pt wire 'couple. Therefore, the galvanometer scale was calibrated by placing a glass substrate with the fired 'couple in a muffle furnace and calibrating it against a commercial thermocouple. However, it was found that this calibration curve was in good agreement with the theoretical curve obtained from the standard temperature-E.M.F. tables.

The substrate, heating block and contacts to the substrate were mounted on a 1/4" thick Mycalex sheet which was rigidly fixed above a similar Mycalex sheet upon which was mounted the electronic heater. The collimating apertures and a shutter (T in Figure 2.1) were situated between these two sheets. The substrate and the collimating apertures were at the same potential as the crucible to prevent any metal ions, which may have formed in the source region, being accelerated towards the substrate.

The contacts having been fired on to the surface previously, the glass substrates were washed prior to being used in the detergent 'Teepol', rinsed, dried and polished with lens tissue. The crystalline substrates were cleaved and the contacts fired on to the surface. As these substrates could not be cleaned by the above method they were handled with care to prevent contamination of the surface until they were required.

The required substrate was placed in position and the whole arrangement, as shown in Plate 2.1, was enclosed in the working chamber of a vacuum unit. The electrical and mechanical connections were made through the base plate. The substrate surface was given a final clean by a glow discharge from aluminium electrodes and this discharge also outgassed the vacuum chamber. When a pressure of 10^{-5} mm. Hg. was reached in the chamber, the crucible and its contents were outgassed by heating to above the melting point of the metal charge. During this outgassing the substrate was protected by the shutter. The substrate was then heated to a suitable temperature and, with the shutter removed, the crucible temperature was raised slowly until condensation of the metal film just began. At this point the thermocouple readings for the crucible and the substrate were noted.

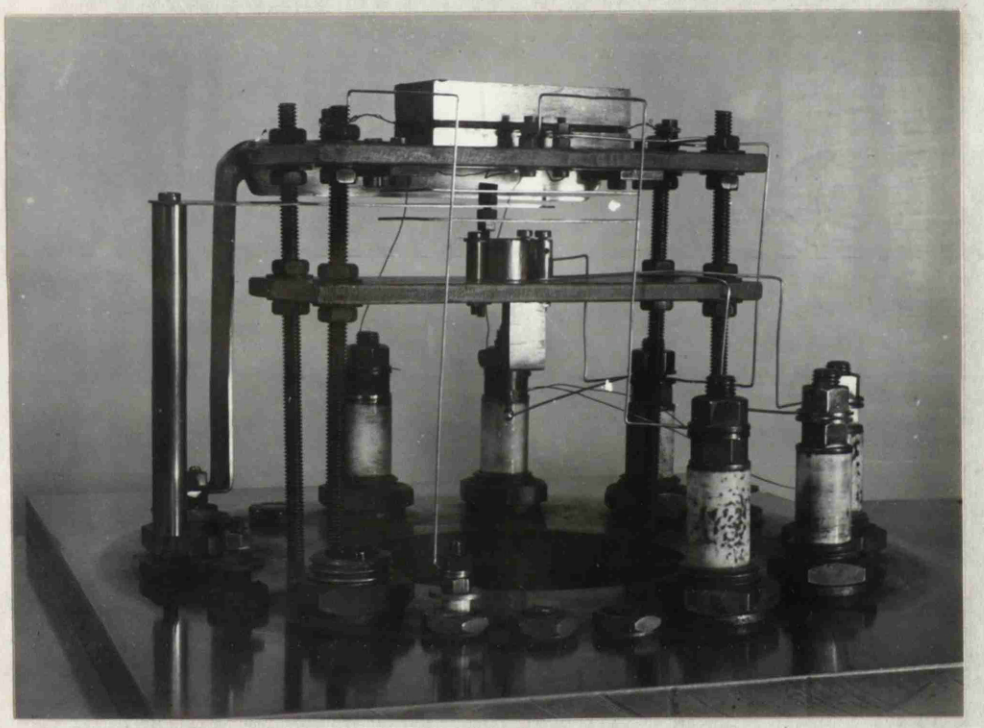


Plate 2.1. Apparatus for the determination of adhesive energy mounted in the working chamber of a vacuum unit.

Recharging of the crucible was facilitated by unclamping the whole crucible mounting.

3. Results

The conditions for condensation of a number of metals on various substrates were examined and the results are shown in Figures 2.4, 2.5 and 2.6. From these results the heats of condensation A were found for Al, Ag and Cd on glass, and Al and Ag on the (100) faces of NaCl and KBr. The conditions for condensation of Cr on these substrates were also examined but it was found that this metal sublimated and this prevented the use of the relationship between the crucible temperature and the pressure of the metal vapour stream given by Kelley[30].

Also shown in Figures 2.4 and 2.5 are the conditions for condensation of Al on glass and (100) NaCl obtained by Rhodin. It can be seen that there is no agreement between these results and those of the present investigation. In both cases the values of A found by Rhodin are much higher. At first it was thought that the substrates used in the present work might have been contaminated during the firing of the silver contacts on the surfaces to be used for the indication of the formation of the films. Therefore, trial runs were made without using silver contacts, the resistance probes being pressed

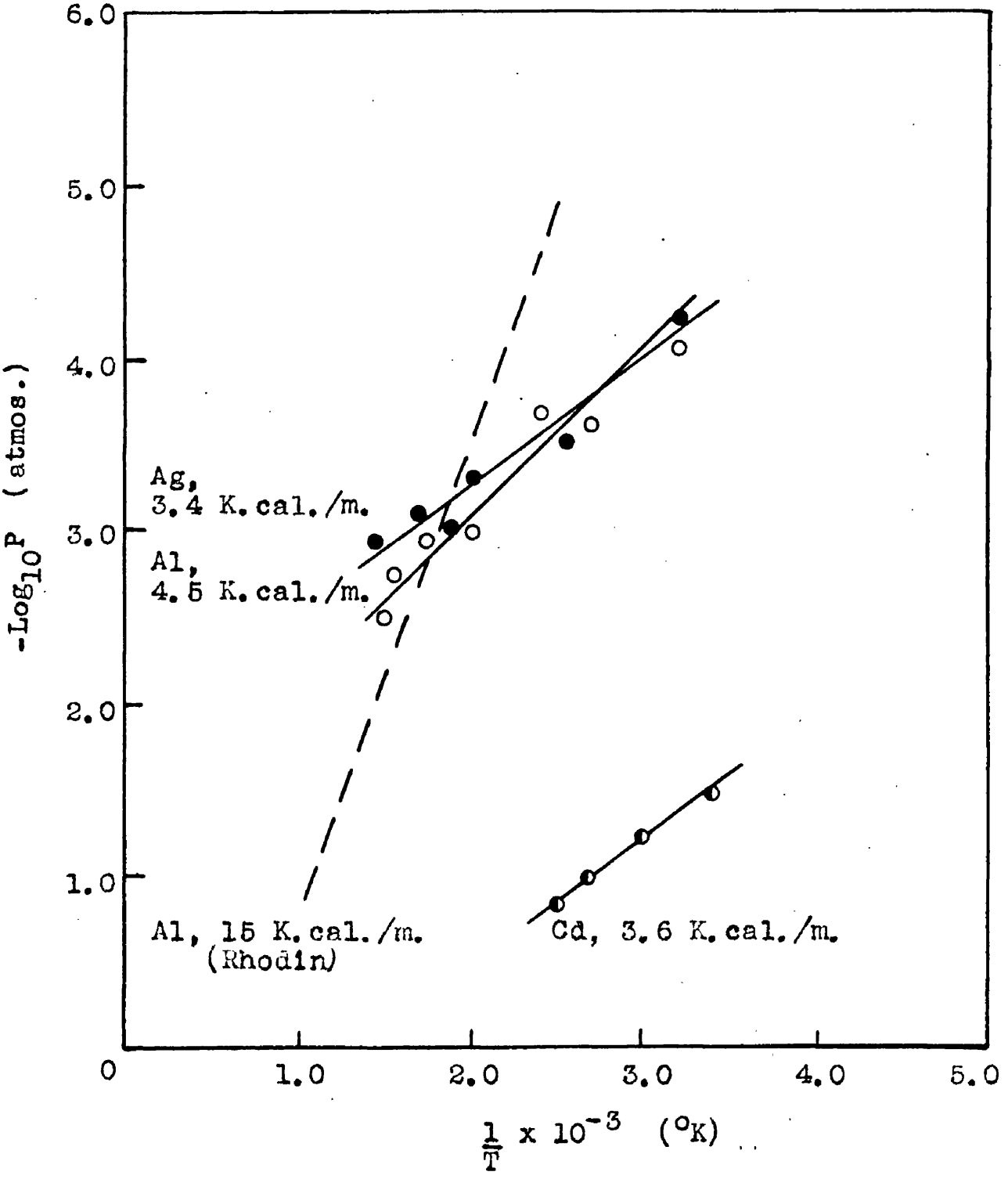


Figure 2.4. Condensation conditions for metals on glass.

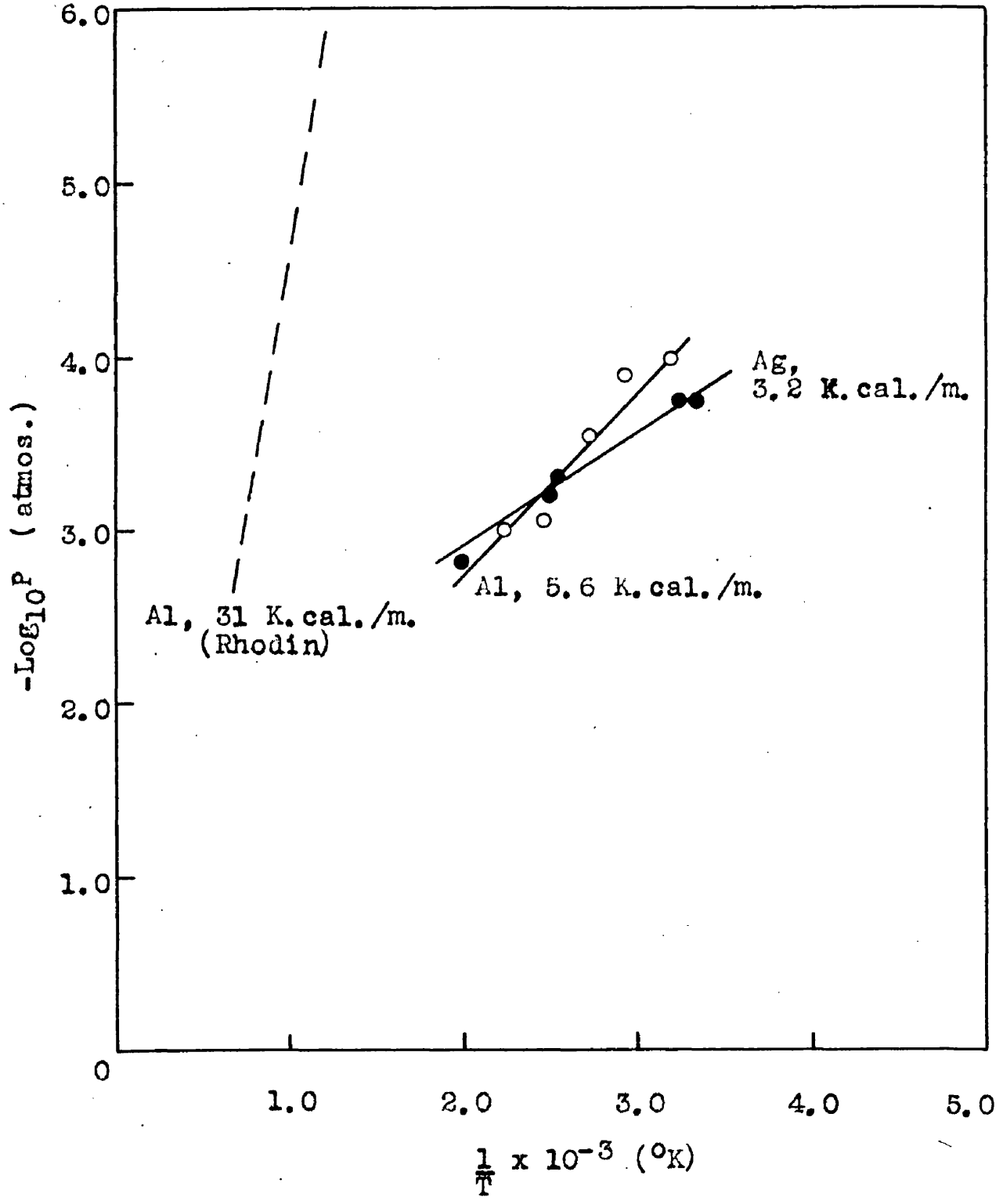


Figure 2.5. Condensation conditions for metals on the (100) face of NaCl.

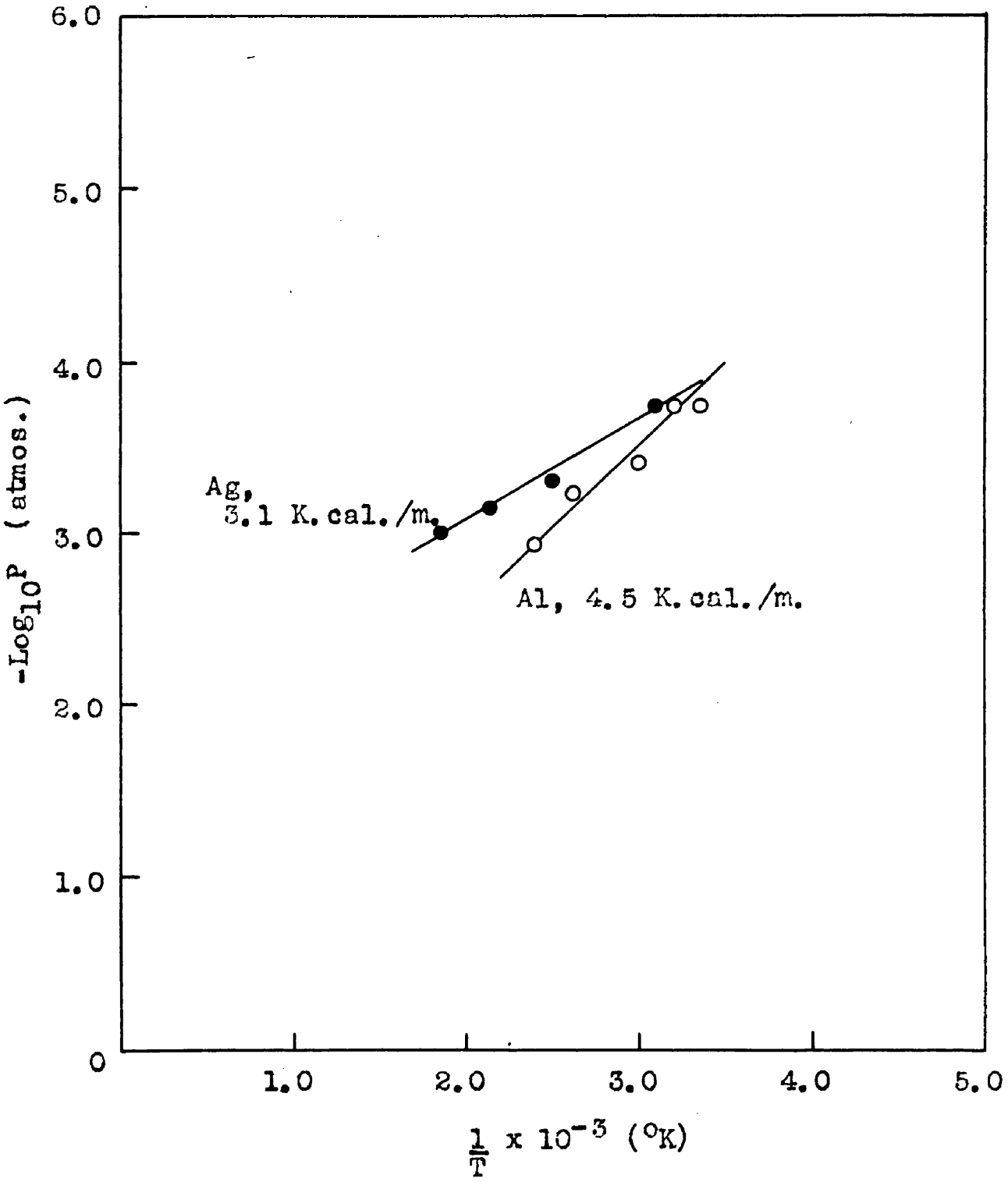


Figure 2.6. Condensation conditions for metals on the (100) face of KBr.

directly on to the substrate surfaces. However, the results obtained in these trial runs were the same as before; in fact, no matter what precautions were taken, no condensation of Aℓ on glass or NaCℓ was found to occur under the conditions given by Rhodin. Further examination of Rhodin's results show that the condensation of Aℓ occurred at higher substrate temperatures than those observed in the present work and the discrepancy in the results could be due to over-heating of the thermocouple probe on the substrate by radiation from the source. In the present investigation the substrate temperature was, in most cases, measured by a thermocouple fired on to the surface and this type of 'couple would not be affected by radiation. However, as can be seen in Figure 2.2, care was taken that the thermocouple was well shielded from radiation in all cases.

In the case of Rhodin's results for Aℓ on (100) NaCℓ, it was found that, if the graph was extrapolated to a substrate temperature of 20°C., the aluminium should condense on the surface at a very low vapour stream pressure; in fact, this pressure corresponded to a source temperature which was less than the melting point of aluminium. This condition could not occur unless the aluminium sublimated and sublimation was certainly not observed in the present investigation. Furthermore, the values found by Rhodin for the heat of condensation A for Aℓ on glass and (100) NaCℓ

of 15 K.cal./mole and 31 K.cal./mole respectively, are very high and would, in fact, indicate chemisorption. It will be shown later, particularly with Al on NaCl, that there is no evidence of a chemical reaction between aluminium and these surfaces.

An indication that the method employed in the present investigation was reliable is given by the work of Estermann[31]. In a study of the heats of evaporation of metals from surfaces, the value for cadmium on glass was given as 3.5 K.cal./mole. The heat of evaporation can be defined as the energy between an atom and the surface plus the energy between two atoms or a doublet and this is similar to the definition of A. The value of A for cadmium on glass obtained in this investigation was 3.6 K.cal./mole which compares very favourably with the value given by Estermann.

Having now obtained values for A, the adhesive energy E, can be calculated by determining the cohesive energy in the first layer of the metal Δ. Rhodin made a crude approximation for Δ and, in the case of aluminium on glass, obtained a value of 15 K.cal./mole which gave zero energy between the film and the glass substrate. Though the adhesion between aluminium and glass may be small, it was felt that the result of Rhodin was exaggerated. Therefore, it was decided that a theoretical calculation of

E would be more profitable than a crude approximation of Δ and these theoretical values could then be compared with the experimental values of A which should be slightly greater.

4. A Theoretical Determination of the Energy of Adhesion

The condensation of the first layer of metal on the substrate can be considered to be similar to the physical adsorption of a gas on a surface by van der Waals' attractive forces. There are three electrostatic effects which jointly account for these forces: the orientation effect of Keesom[32], the induction effect of Debye[33], and the dispersion effect of London[34]. This dispersion effect accounts for the attraction between a fluctuating dipole and an induced dipole and is the most important of the three effects.

London showed that the dispersion potential between an isolated atom and an atom of the adsorbing medium was given by

$$E = -\frac{C}{r^6}$$

where r is the equilibrium distance and C is the dispersion constant having the value

$$C = \frac{3}{2} aa' \frac{JJ'}{J + J'}$$

where a and a' are the polarizabilities of the metal atom and the substrate atom respectively, and J and J' are their characteristic energies.

The interaction between the metal atom and the entire surface of the substrate can be calculated by an integration over the atoms of the substrate surface, assuming that the distance between the metal atom and the surface is not smaller than the distance between the atoms in the surface. London has given the mutual dispersion energy between an infinitely large surface and an isolated atom as

$$E = -\int \frac{C}{r^6} N dv = -\frac{N\pi}{6r^3} . C$$

where N is the number of adsorbing atoms per unit volume in the substrate and dv is the volume element.

An exact evaluation of the above equation is not possible since the characteristic energies of most metals are not yet known. However, London[35] has shown that for a first approximation, the ionization potentials of the atoms may be used in place of the characteristic energies.

Metals on Glass

Due to the amorphous nature of glass only an

approximate value of N could be obtained and this was achieved by considering the crystalline silica network described by Zachariasen[36]. The oxygen ions were taken to be the adsorbing ions since their polarizability is far greater than that of the silicon ion. Figure 2.7 shows the position of the oxygen ions in the network and the lattice dimensions. The distance between the two layers is also shown. From this arrangement, a cell of dimensions $(3 \times 2.6) \times 4.5 \times 4.24$ A^3 contains a total of nine oxygen ions, that is, $N = 0.605 \times 10^{23}$ per $cm.^3$.

The polarizabilities of ions were taken from Van Vleck[37], but the polarizabilities of uncharged atoms were calculated from

$$a = \frac{e^2}{4\pi^2 m v_o^2}$$

where v_o is the characteristic frequency of the atom and the other symbols have the customary significance. The characteristic frequency of an atom is the frequency of a single oscillator substituted for all the oscillators that make up the atom. For an uncharged atom to be polarized, an electron must be displaced so that it lies between the first excitation level and the first ionization level. In most cases, these two levels are very close and, hence, for

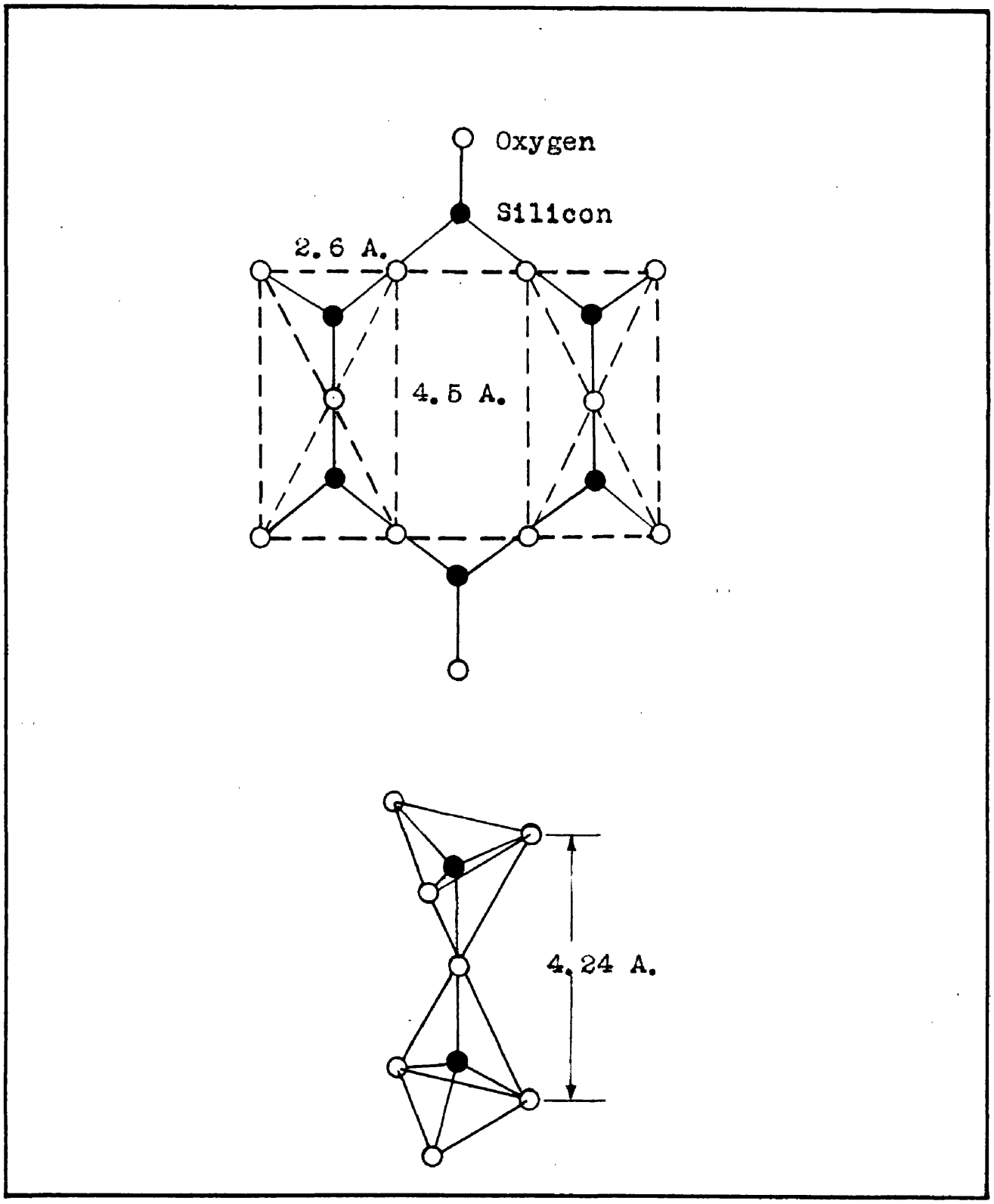


Figure 2.7. Diagram of the crystalline silica network after Zachariasen showing the lattice parameters.

a first approximation, the characteristic frequency can be taken to correspond to the first ionization potential, that is

$$I = h\nu_o$$

where h is Planck's constant and I is the ionization potential. Values of I were obtained from Finkelburg and Humbach[38].

The equilibrium distance, r, was taken as the mean of the distances of closest approach of the atoms in the metal and the ions in the substrate.

The adhesive energy calculated by this method is shown in Table 2.1 for a number of metals on glass. It can be seen that the value of E for aluminium is 3.4 K.cal./mole instead of the value of zero, as supposed by Rhodin. The results of this calculation appear to be of the right order since, when compared with the experimental values of **A**, the values of E are always slightly less than these values of **A**, which is as it should be.

It should be mentioned here that there appears to be a discrepancy between some of the values found by Rhodin and those calculated in this work. For example, in the calculation of the dispersion constant between an aluminium atom and an oxygen ion, Rhodin obtained a value of

TABLE 2.1

The theoretical adhesive energy (E) for metal films on glass

Metal	a 10^{24} cm.^{3}	I 10^{12} ergs	C 10^{60} ergs.cm.^{6}	r A	E K.cal./m.	A K.cal./m.
Al	3.04	9.60	153	2.73	3.4	4.5
Ag	1.90	12.15	117	2.75	2.8	3.4
Cd	1.35	14.40	97.0	2.79	2.0	3.6
O^{2-}	3.88	88.0				

321×10^{-60} ergs cm.^{6}. This value is three times greater than that found in this work. A small part of the discrepancy is due to the fact that Rhodin has taken a value for the ionization potential of an oxygen ion as 20.5×10^{-12} ergs, but the ion is doubly charged and should therefore have an ionization potential of 88.0×10^{-12} ergs. However, the major part of the discrepancy appears to lie in the value of the polarizability used for the aluminium atom. Rhodin has used a value for this which is approximately three times greater than the value used in this work which was calculated from the first ionization potential.

Metals on Crystal Faces

The most favourable position for adsorption on the (100) face of an alkali halide is the centre of a unit cell since there is a potential well at this position. This potential well can be seen from the potential energy surface of the (100) face of NaCl which was constructed after Orr[39] and is shown in Figure 2.8. If a metal atom is adsorbed in this position then the polarizabilities and the characteristic energies of both the anion and the cation of the crystal surface must be considered. Mayer[40] has given values for the lattice energy characteristics and polarizabilities for the alkali halides.

The equilibrium distance, r, is dependent on the

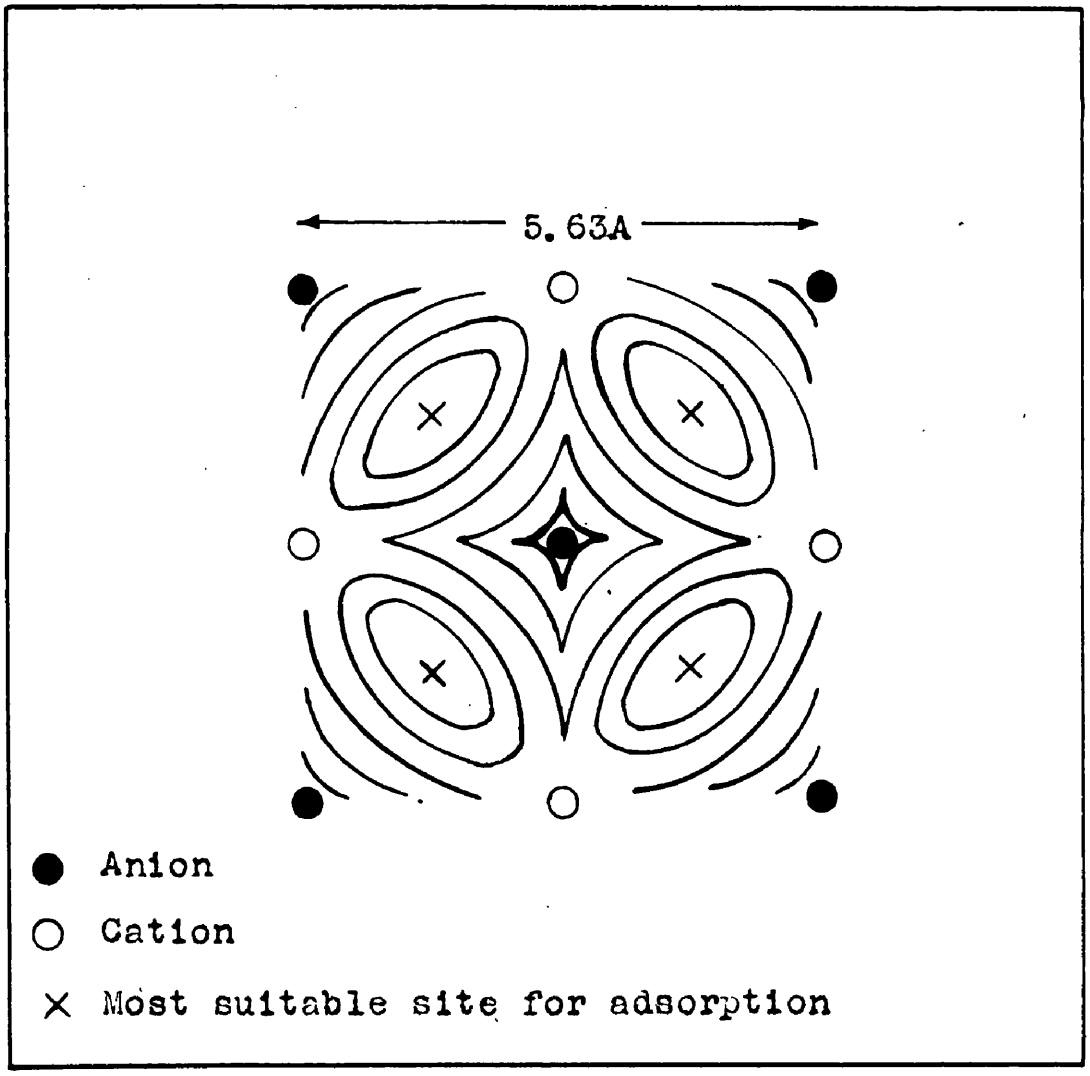


Figure 2.8. The potential energy surface of the (100) face of NaCl.

size of the cation since it has a larger radius than the anion. Knowing the distance between cations and the radius of the cation and the metal atom, the distance r can easily be evaluated. The value of N is also simple to determine.

Table 2.2 gives the adhesive energy between the metals, aluminium and silver, and the substrates, NaCl (100) and KBr (100). Once again it can be seen that these values are less than the values of A obtained experimentally.

The binding energy for aluminium on NaCl (100) is the only case where direct comparison with the theoretical values of Rhodin can be made and again it was found that the value obtained by Rhodin was three times greater than the value calculated in this work. Again the discrepancy would appear to be due to the value taken for the polarizability of aluminium.

5. Conclusions

The experimental investigation into the heat of condensation of metals on various substrates appeared to give reliable results. However, this method was limited to metals with relatively low melting points since the crucible temperatures could only be measured up to 1500°C. It was hoped to use an iridium-rhodium/iridium thermocouple for the measurement of higher temperatures but unfortunately

TABLE 2.2

The theoretical adhesive energy (E) for metal films on the (100) face of NaCl and KBr

Metal/ Substrate	a' 10^{24} cm.^{3}	I' 10^{12} ergs	C 10^{60} ergs.cm.^{6}	r A	E K.cal./m.	A K.cal/m.
Ag/NaCl	3.27	16.4	65.1	2.00	2.7	3.2
Al/NaCl	3.27	16.4	90.4	2.00	3.8	5.6
Ag/KBr	5.22	14.2	97.5	2.02	2.5	3.1
Al/KBr	5.22	14.2	136	2.02	3.5	4.5

when this thermocouple was finally obtained it was found to be too brittle to be used in the apparatus. However, these limited experimental results indicated that the method of calculating the theoretical adhesive energy gave values which were of the right order of magnitude.

It will be seen later that the adhesive energy for a wide range of metal films on glass and crystal substrates, calculated by this method, were compared with the results of the experimental investigation of adhesion using an apparatus described by Heavens. This comparison gave an indication of the mechanism causing adhesion between the films and the substrates.

CHAPTER 3

DEPOSITION OF THIN FILMS

1. Introduction

Thin films can be deposited in vacuum by two methods, namely, evaporation and cathodic sputtering. The material to be deposited by evaporation is heated in a chamber exhausted to a pressure of 10^{-4} mm. of mercury or lower. The vaporized material can then leave the source relatively unimpeded by air or other gas molecules and move in straight lines to condense on the substrate surface. The technique of sputtering employs an electrical discharge at a pressure of the order of 10^{-2} mm. of mercury. The ion bombardment of this discharge tears away particles from a cathode made of the material to be deposited. The particles diffuse through the discharge to condense on the substrate surface. Only metals can be used as the cathode material but by controlling the residual gas in the chamber films of either a metal or a metallic compound can be deposited.

In both methods the structure and properties of the film are dependent upon the conditions under which they

are deposited. The more important conditions which are liable to influence the formation of a thin film are: the condition of the substrate surface, the rate of evaporation and the residual gas. The majority of the thin films examined in this investigation were deposited by evaporation and a standard procedure was adopted to control the influence of the above conditions.

2. The Substrate Surface

The cleanliness of the substrate surface is of prime importance in the investigation of adhesion. A contaminating surface layer would prevent the short range attractive forces of the substrate influencing the condensing metal atoms.

Where the substrate was a crystalline material, a fresh flat surface was exposed by cleavage immediately before use and the substrate was placed directly in the evaporation chamber. This procedure prevented gross contamination of the surface. Glass and plastic substrates were selected to have a very smooth surface and this surface was subjected to a fairly vigorous cleaning process. The surface was first washed with cotton wool soaked in the detergent 'teepol'. This removed a large amount of grease contamination due to handling. The surface was then

thoroughly rinsed in water, dried with cotton wool, and finally polished with lens cleaning tissue. This technique gave a reasonably clean grease-free surface.

Both types of substrate surface were subjected to a cleaning process under vacuum. An electrical glow discharge was passed through the evaporation chamber for approximately ten minutes at a pressure of 10^{-1} - 10^{-2} mm. Hg. The ion bombardment from this discharge removed any final contamination which might be adhering to the surface.

In all cases the films were deposited on the substrates at room temperature. Overheating of the substrate by the source was prevented by a large source to substrate distance and a rapid rate of evaporation.

3. The Rate of Evaporation

Many workers, notably Levinstein[5] and Sennett and Scott[41], have shown the effect of varying the rate of evaporation on the structure of thin films. This variation alters both the velocity at which the atoms arrive on the substrate and the intensity of the vapour beam. From the above work it appears that the variation of the intensity of the vapour beam is the important factor, the aggregation in the film structure tending to decrease as the intensity increases. Therefore, the rate of evaporation was considered

to be an important experimental condition and was recorded for each film deposited.

4. The Residual Gas

When discussing the influence of the residual gas the pressure and the nature of the gas must be considered.

For a film to be deposited by evaporation, the mean free path of the vaporized atoms must be large compared with the source to substrate distance. In the apparatus to be used in this investigation this distance was 25 cm. and, by working at pressures of 10^{-4} - 10^{-5} mm. Hg., the mean free path of the metal atoms would be 30-300 cm. Therefore, the metal atoms would make very few collisions with the residual gas molecules on their journey from source to substrate.

At the above pressures the number of residual gas molecules striking the substrate surface is not small compared with the rate of condensation of the metal atoms. Contamination of the deposited film may occur especially if the condensing atoms have an affinity for the residual gas. The most harmful constituent of the residual gas normally present in a continuously evacuated system is oxygen. To minimise the contamination of films in this investigation, the metal to be deposited was heated with a shutter shielding the substrate surface. If the vaporized metal reacted with

the residual oxygen, there was a drop in the gas pressure due to gettering. If the shutter was then removed and the film rapidly deposited, the degree of film contamination was reduced. This preliminary heating of the source and the use of a shutter also prevented any contamination on the source or the metal charge from reaching the substrate. Starting and stopping the formation of a film by use of a shutter assisted in the estimation of the rate of evaporation.

5. Evaporation Sources

The metal to be evaporated must be heated in a suitable source and the shape and material used for the source depend upon the metal. The metal may be in the form of wire, foil or chips, and may wet, or even alloy with, the source material. There are two simple types of source both of which were used. The first is a boat or trough pressed out of sheet material, and the second is a conical basket wound from wire. These sources were heated by passing a high electric current through them. The material used for the source must have a high melting point and a low volatility and the most commonly used materials are tungsten, tantalum and molybdenum. If the metal to be evaporated forms an alloy with the source material, the source is liable to be completely dissolved. To prevent

this the volume of the source material must be kept large compared with that of the metal. The use of multi-strand wire helps in this problem. Figure 3.1 gives an idea of the shapes of the sources used while Table 3.1 gives details of the techniques used for evaporating the wide range of metals.

6. Apparatus

A large bell jar, 36 cm. in diameter and 66 cm. in height, was used as the working chamber. The bell jar, sealed to a heavy baseplate by a fitted rubber gasket, was evacuated by the vacuum unit shown in Figure 3.2. Mounted directly below the baseplate was a flap valve and a 2" Metrovac oil diffusion pump. The main pumping line ran from a two stage Metrovac rotary pump on anti-vibration mountings at the bottom of the unit through a metal phosphorous pentoxide trap to a vacuum stopcock at the top of the unit. Side connections from this pumping line passed through valves directly to the chamber and to the backing side of the diffusion pump. Pressure gauges, rotating seals, insulated electrodes, and the air leak valve were connected directly to the working chamber by means of plugs in the baseplate. These plugs were fitted into machined holes counterbored on the underside of the baseplate and were tightened down on to O-rings by nuts on the upperside.

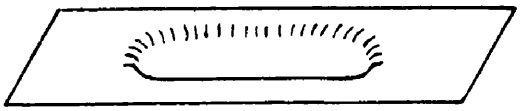
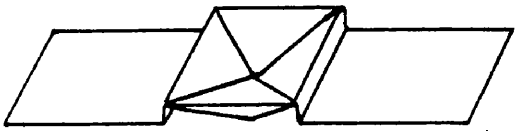
	Molybdenum boat pressed out of 0.1 mm. sheet.
	Tantalum boat made out of 0.1 mm. sheet.
	Tungsten basket wound from single strand 1 mm. wire or three strands of 0.5 mm. wire.

Figure 3.1. Description of evaporation sources.

TABLE 3.1

The evaporation techniques for various metals

Metal	Form	Source	Remarks
Aluminium	Wire	W stranded basket	Alloys with W
Cadmium	Chips	Mo boat	
Chromium	Chips	W basket	
Copper	Foil	Ta, Mo boat	Does not wet source
Gold	Wire	W basket	Partially wets source
Iron	Wire	W stranded basket	Alloys with source
Lead	Foil	Mo boat	Does not wet source
Magnesium	Wire	W basket	
Manganese	Chips	W basket	
Molybdenum		Mo wire	
Nickel	Wire	W stranded basket	Alloys with source
Silver	Wire	Mo boat	
Tin	Foil	Ta boat	
Titanium	Chips	W basket	Alloys with source
Zirconium	Chips	W basket	Alloys with source
Zinc	Chips	W basket	

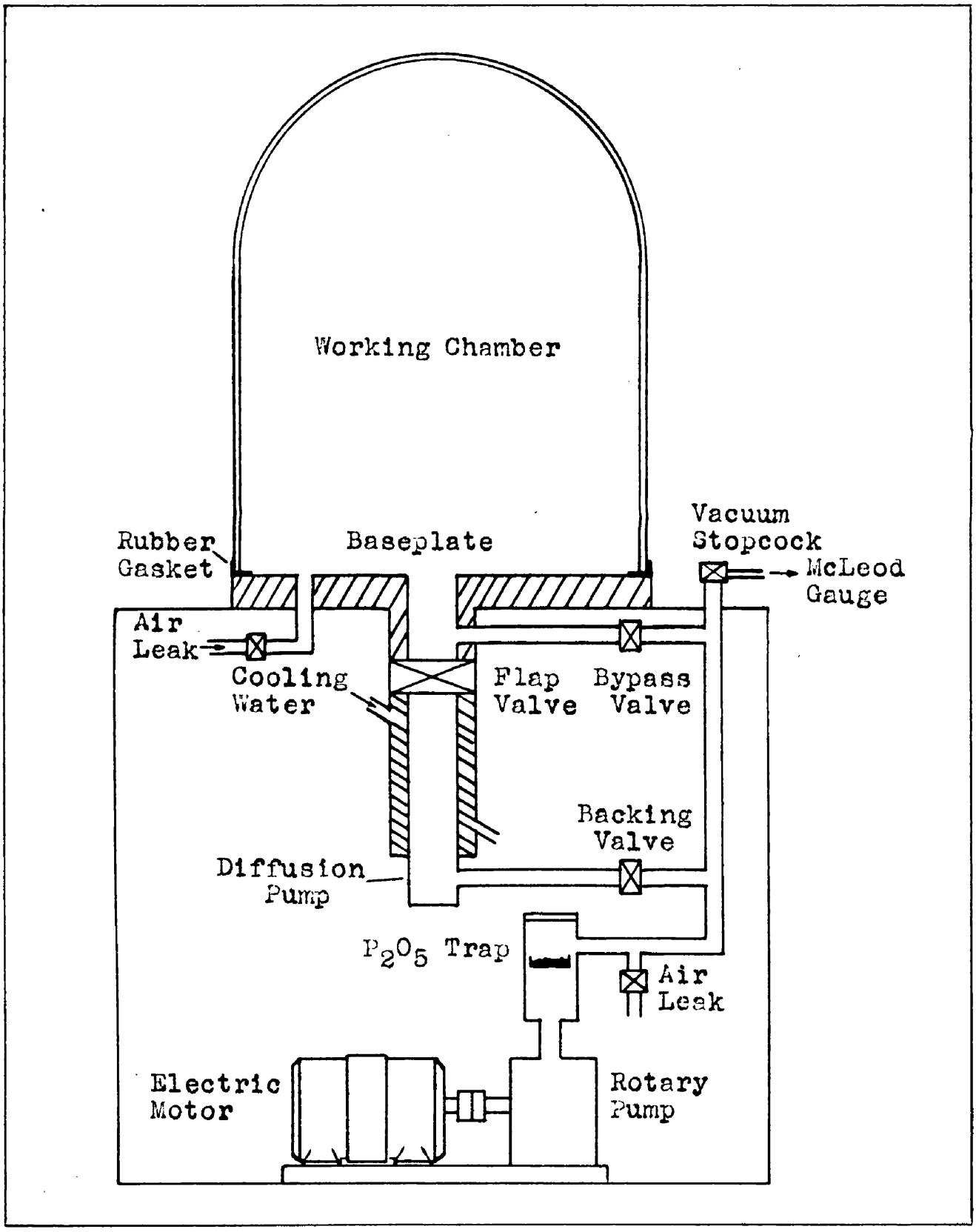


Figure 3.2. The vacuum unit.

Pressures in the working chamber were measured by a McLeod gauge and a hot filament ionization gauge. The McLeod gauge, connected to the vacuum stopcock, measured pressures down to the order of 10^{-3} mm. Hg. and was used for the initial evacuation of the chamber by the rotary pump. The ionization gauge, connected directly to the working chamber, measured the final pressure obtained by the diffusion pump.

The glow discharge electrodes were made from aluminium, a metal with a low rate of sputtering. The electrodes were connected through insulated plugs in the baseplate to a high voltage power supply. The supply of approximately 2 kilovolts was controlled by a Variac. This glow discharge not only cleaned the substrate surfaces but also cleaned and outgassed the walls of the working chamber allowing the final pressure to be reached in a shorter time.

The evaporation sources were clamped to heavy brass blocks bolted to insulated plugs in the baseplate. The sources were heated by passing a current of 0-60 amperes through them from a low voltage transformer controlled by a Variac.

It was proposed to measure the thickness of each film deposited and therefore a glass blank was situated beside the substrate to collect an identical film. The

thickness of the deposit on this glass blank was measured by multiple-beam interferometry. To ensure that the thickness of the deposit did not vary over the substrate and the glass blank, the two surfaces were placed symmetrically above the source at a distance of approximately 25 cm. It has been shown[42] that the thickness variation over quite a large area at this distance from the source would be negligible. The surfaces, having received a deposit of the specimen film, were then rotated so that the film on the glass blank received a highly reflecting coating over one edge which is required for the thickness measurement. This was achieved by the following turn-table device controlled from outside the chamber.

A perspex disc, 1/4" thick and 10½" in diameter, was rigidly fixed 30 cm. above the baseplate. A second disc of the same dimensions was placed on top of the fixed disc and could be rotated by a geared mechanism through a Wilson seal in the baseplate. Two slots, 3" x 1", were cut in the upper disc to hold the substrate material and the glass blank. Glass and plastic substrates were usually of this size and were held in the slots close to the lower disc by shim brass pieces. The crystalline substrates, being smaller, required a secondary holder which could easily be slipped into the 3" x 1" slot. Windows were cut in the

lower disc at appropriate positions above the evaporation sources and the shape and size of these windows determined the area on which the film was deposited. In order that the impinging atoms of the evaporate should not be interfered with in any way, the edges of the windows of the lower disc were chamfered. This also gave a sharp edge to the films which was required for the future thickness measurements. Figure 3.3 shows a cross-section through the upper and lower discs and Figure 3.4 shows a plan view of the holder for the small substrates. A general view of the working chamber is given in Plate 3.1.

7. Cathodic Sputtering

The apparatus for the deposition of a film by cathodic sputtering is shown in Figure 3.5. The working chamber was small, being the top of a dessicator 20 cm. in diameter and 15 cm. in height. The cathode, in the form of a circular disc, was attached to a heavy brass rod held in the chamber by a rubber bung. The chamber was sealed to a heavy metal baseplate by a rubber gasket and evacuated by a rotary pump capable of giving pressures less than 0.001 mm. Hg. Connections to the chamber were made by plugs as described earlier. The cathode was earthed and the high voltage was applied to the baseplate and controlled

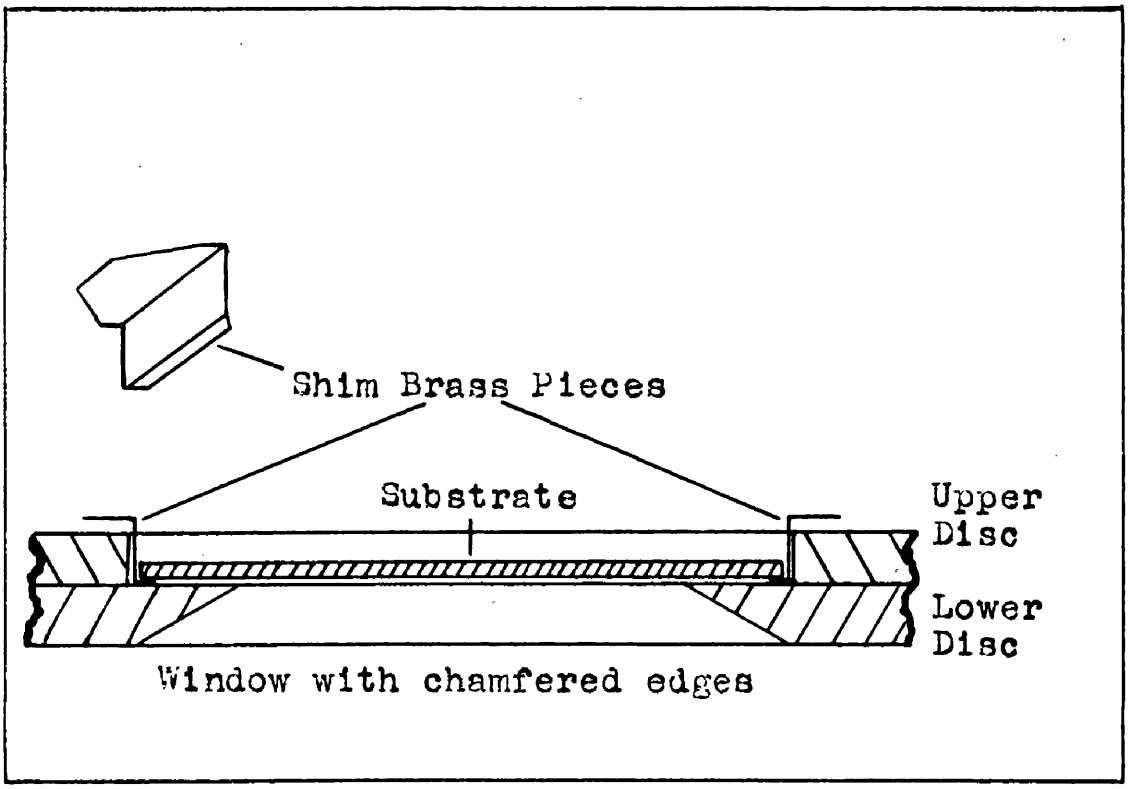


Figure 3.3. Section through upper and lower discs showing the position of the substrate above the window.

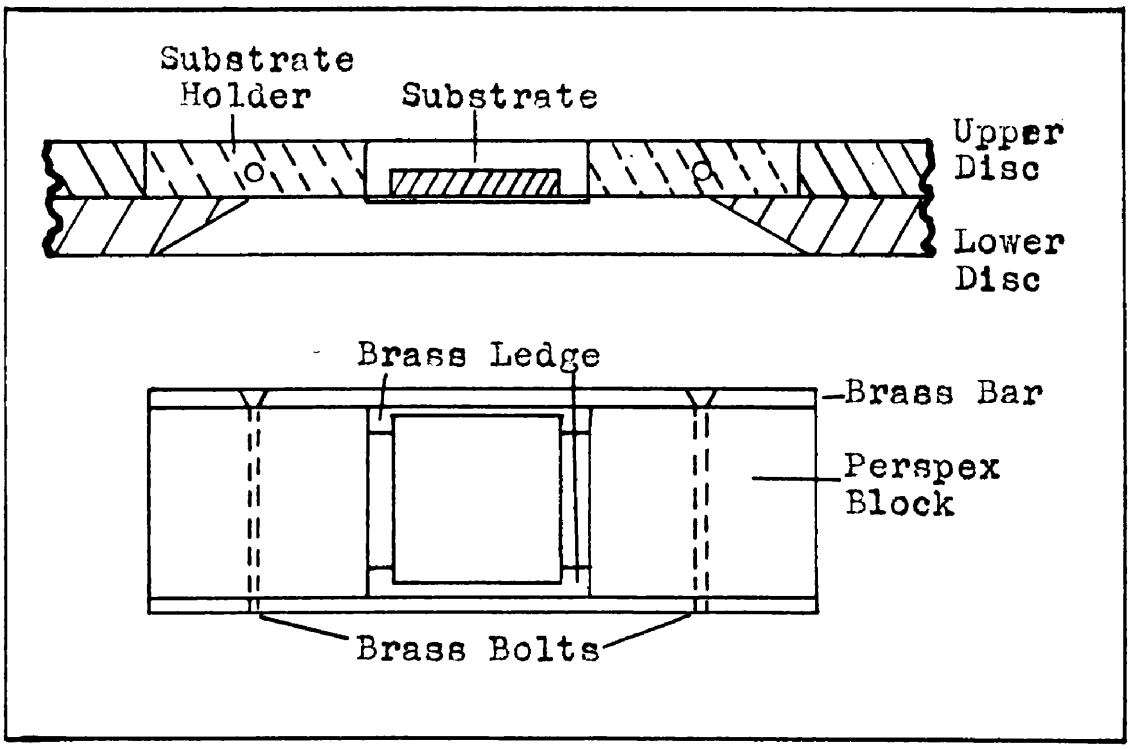
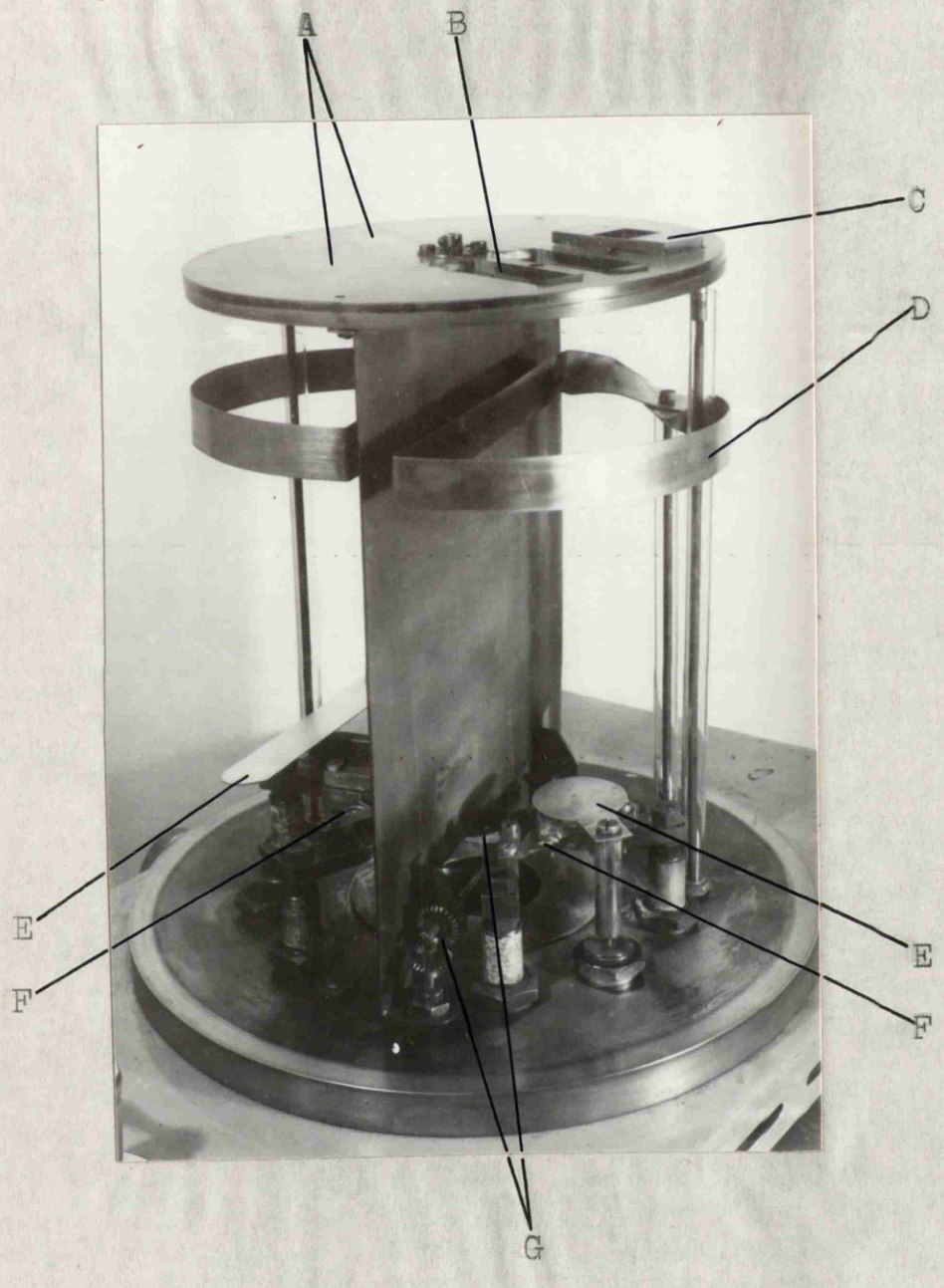


Figure 3.4. Section and plan of substrate holder.



A - Windows in lower rigid disc.
B - Slots for substrates in upper rotating disc.
C - Crystal substrate holder.
D - Glow discharge electrodes.
E - Shutter.
F - Evaporation source.
G - Gearing mechanism.

Plate 3.1. The working chamber.

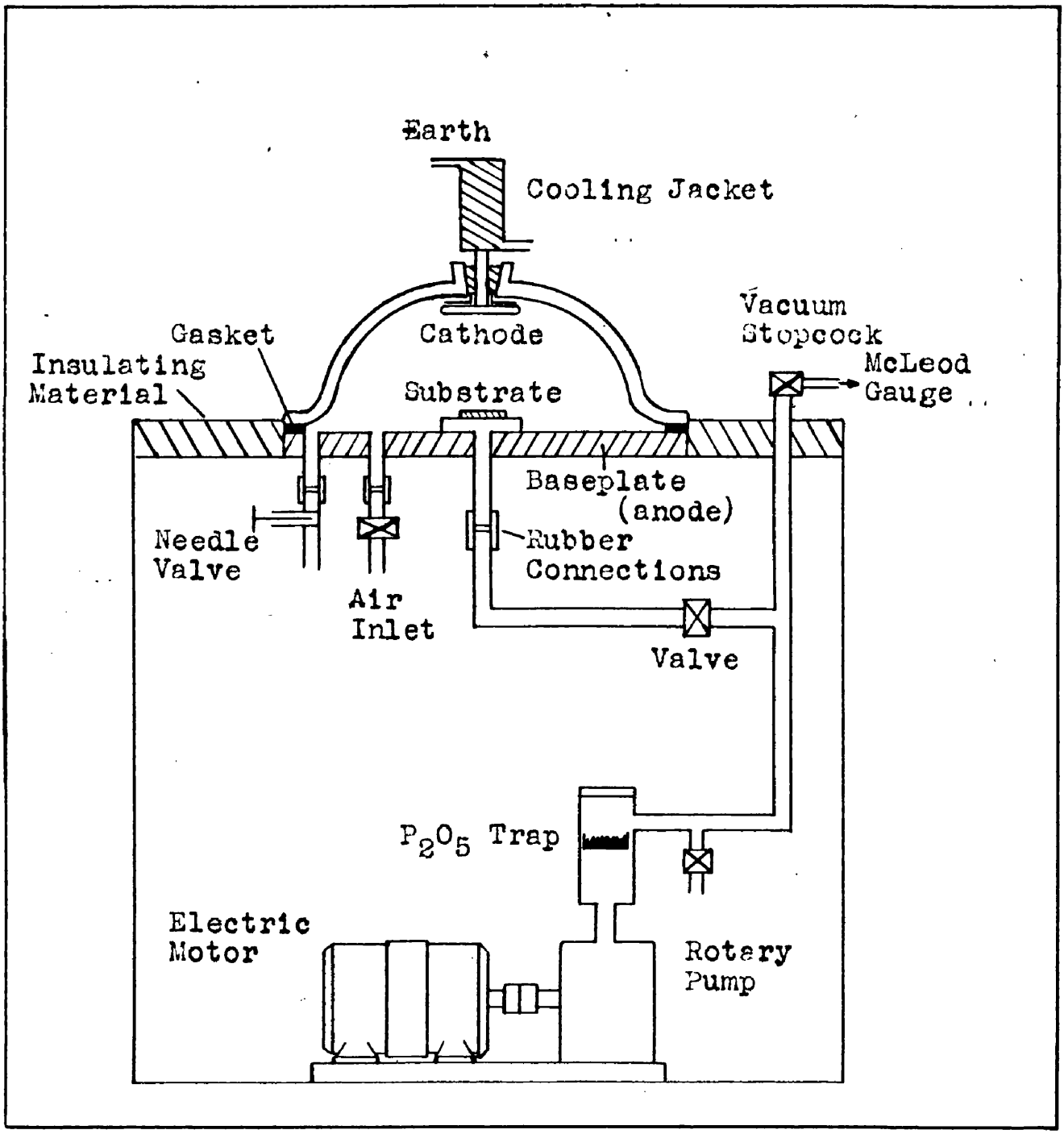


Figure 3.5. The sputtering unit.

by a Variac. The main pumping line and the air inlet valves were insulated from the baseplate by rubber connections and further insulating material round the baseplate prevented it being touched when the chamber was in position. The pressure in the chamber was measured by a McLeod gauge attached to the vacuum stopcock and a Pirani gauge connected directly to the chamber.

When a metal is sputtered, the particles leaving the cathode surface may reach the substrate surface as free atoms or in chemical combination with residual gas molecules. This depends on the nature of the residual gas. Pure metal films can be deposited by having an inert residual gas while the metal oxide can be formed by having oxygen or air as the residual gas. If any gas other than air was used in these investigations the chamber was flushed several times with this gas before the final sputtering conditions were reached. The substrate surfaces were prepared in the manner previously described and the substrates were mounted on a metal table 5 cm. below the cathode. The rate of sputtering of a metal depends on the metal, the nature and pressure of the residual gas, and the voltage and current of the discharge, all of which were recorded for each film deposited. Overheating of the substrate and the cathode was prevented by water-cooling the cathode and, where the rate of sputtering of the metal

was slow and excessive heating might occur, the sputtering process was interrupted to allow the cathode to cool.

The conditions under which the metal films to be investigated were deposited have been discussed in detail together with the apparatus for the purpose. Apart from keeping these conditions reasonably constant no elaborate precautions were taken. This has the advantage of closely following the conditions used in laboratory and production techniques and therefore the results of this investigation could be applied to that type of work.

CHAPTER 4

THE MEASUREMENT OF FILM THICKNESS

1. Introduction

As mentioned in the previous chapter, the thickness of each film deposited was measured by multiple-beam interferometry. This technique, developed by Tolansky[43], is now well-established. The film, the thickness of which is to be measured, is deposited on a surface, part of which is covered to give a sharp edge to the film. An opaque metallic highly reflecting layer is then deposited over the edge of the film. The step in this overlayer is measured by using it as one surface of an interferometer and viewing the multiple-beam fringe system in reflection. Provided that the overlayer assumes the exact contour of the surface, this step-height will give the thickness of the film underneath. Tolansky has given adequate evidence that silver fulfils the necessary requirements both in its high reflectivity and its ability to contour the surface.

There are two multiple-beam fringe systems, fringes of equal thickness (Fizeau fringes), and fringes of equal chromatic order. The multiple-beam Fizeau fringe system,

being slightly simpler experimentally, was used in these investigations. In this system, the interferometer is illuminated by a parallel monochromatic beam at normal incidence and the fine dark fringes on a bright background are viewed by a low-power microscope. By adjusting the air wedge between the two surfaces of the interferometer the fringes can be made to cross perpendicular to the step. The displacement of the fringes on crossing the step is expressed as a fraction of the fringe spacing and gives the film thickness in units of $\lambda/2$, where λ is the wavelength of the monochromatic light. However, the quality of the fringe system, that is, the fringe width and the contrast to the background, is influenced by certain factors both in the interferometer and the optical arrangement illuminating it. Tolansky has given detailed attention to all these factors which were taken into account when setting up the apparatus.

2. Apparatus

A diagram of the interferometer is shown in Figure 4.1. The film to be measured was deposited on part of a glass blank, 3" x 1", in such a way that it had a clearly defined edge. An opaque overlayer of silver was deposited over the edge of the film. An optical flat, also

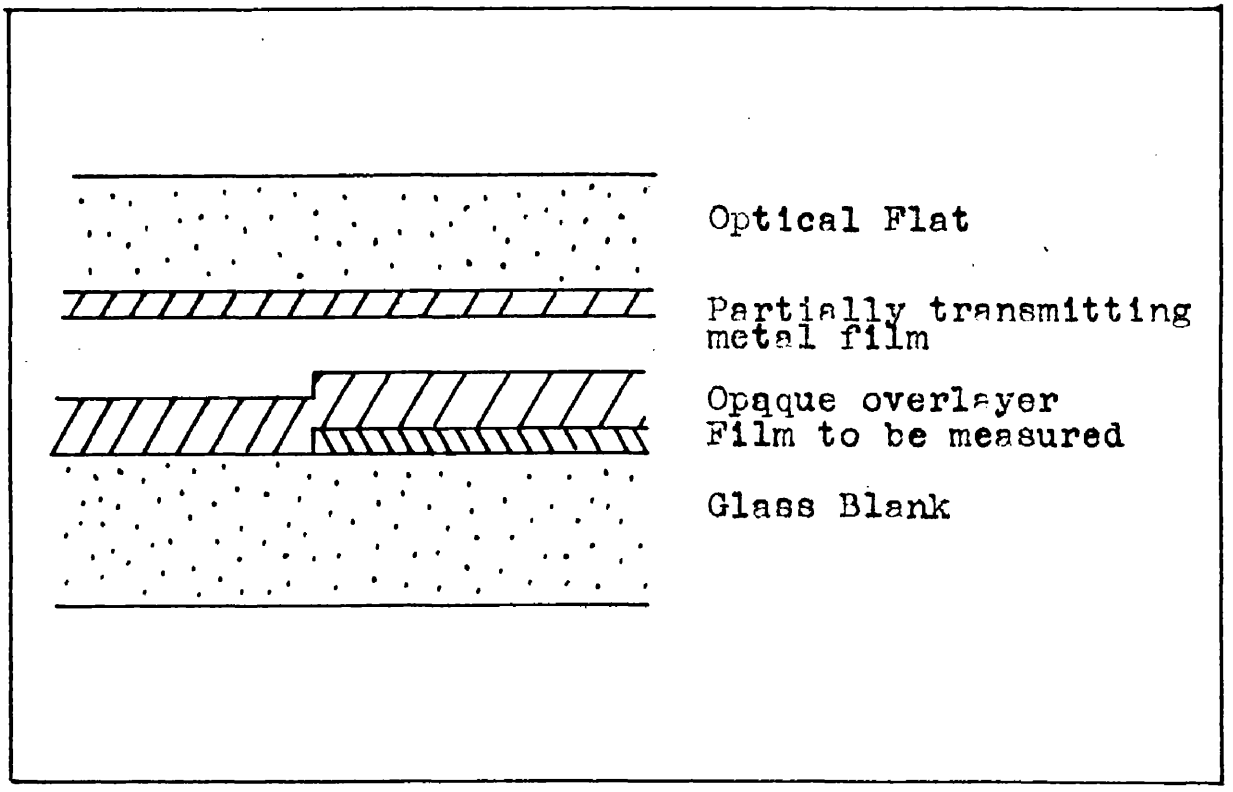


Figure 4.1. Diagram of the interferometer.

coated with a high reflecting, but partially transmitting metal film was placed in close contact with the glass blank to form an interferometer.

The air wedge between the two surfaces of the interferometer, controlling the direction and spacing of the fringes, was formed by the jig shown in Figure 4.2. The optical flat, held by springs against a ledge in the upper plate of the jig, could be pressed against, and tilted relatively to, the other surface of the interferometer, held in the lower plate, by three adjustable screws.

The air wedge should be kept as small as possible for good quality fringes but the factors influencing the quality most are the reflection and the absorption of the coating on the optical flat. By keeping the absorption factor low a high contrast between the maxima and minima of the fringe system is obtained while a high reflectivity gives a narrow fringe width. These conditions were met by using a silver film with an absorption of 5% and a reflectivity of 90%, though later high reflecting multi-layer coatings of negligible absorption were used.

The ideal surface on which to deposit the film to be measured would be an optically polished glass blank but this was not practicable. However, it was found that microscope slides manufactured by Chance were excellent for

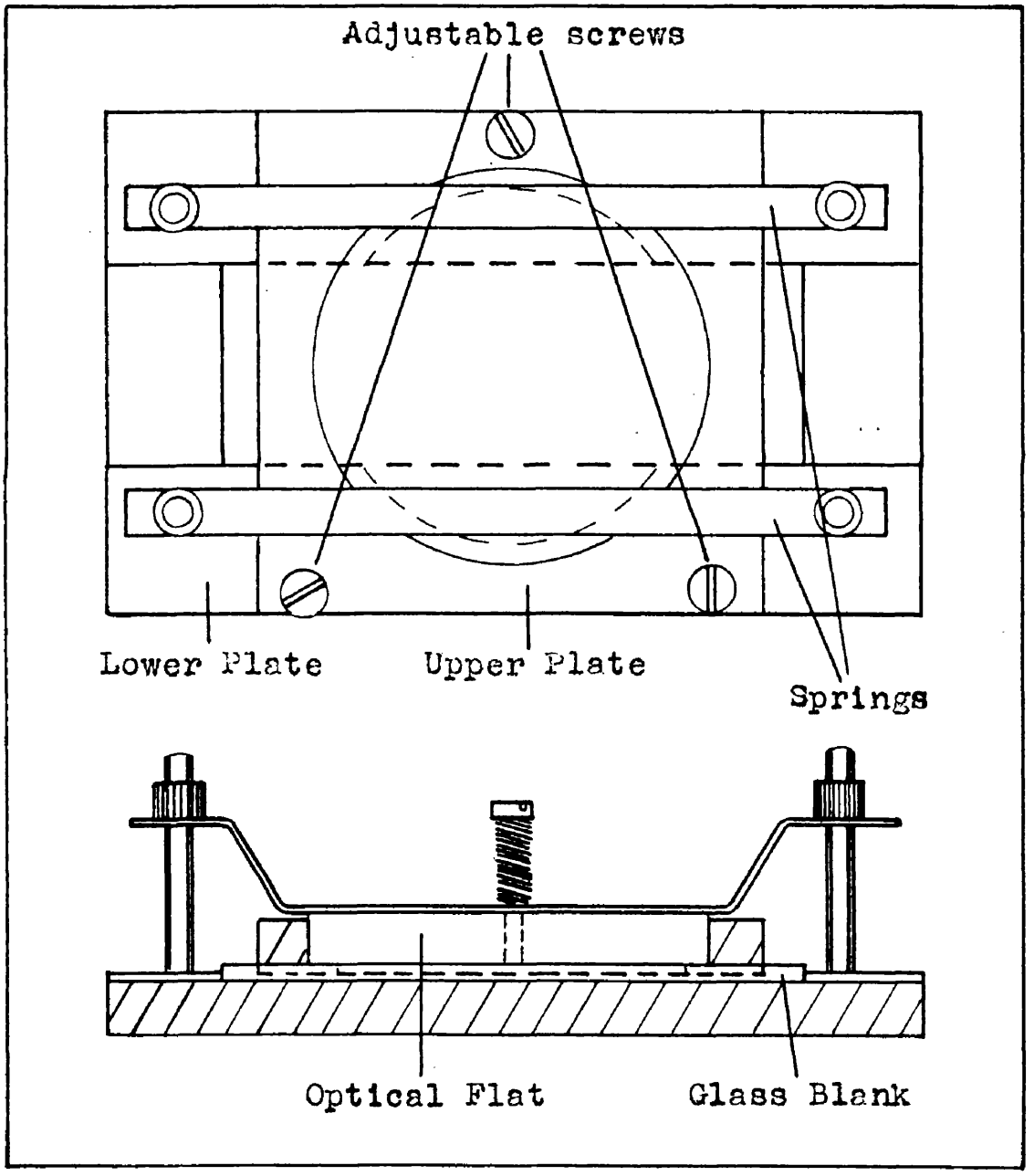


Figure 4.2. Diagram of jig used with the interferometer.

the purpose, having a good surface with only a slight undulation. This undulation, which prevented really close contact between the two surfaces of the interferometer, did not, however, affect appreciably the quality of the fringe system.

The optical arrangement for illuminating the interferometer and viewing the fringe system is shown in Plate 4.1 and diagrammatically explained in Figure 4.3. The source was a Phillips 80 watt mercury lamp, the light from which was focussed on an adjustable diaphragm. The light from this source stop was filtered to obtain the mercury green wavelength at 5461A. The light was then collimated and directed at 90° on to the interferometer. A section of this illuminated area was viewed by a low-power microscope.

Errors in the collimation of the incident beam can affect the quality of the fringe system. The errors depend upon the angular spread of the beam which, in turn, depends upon the size of the source stop. This size is determined by a number of factors such as the number of fringes per centimeter on the surface of the wedge, which gives the separation of the interferometer plates, and the focal length of the collimating lens. The wedge angle determines the numerical aperture of the microscope objective lens since all

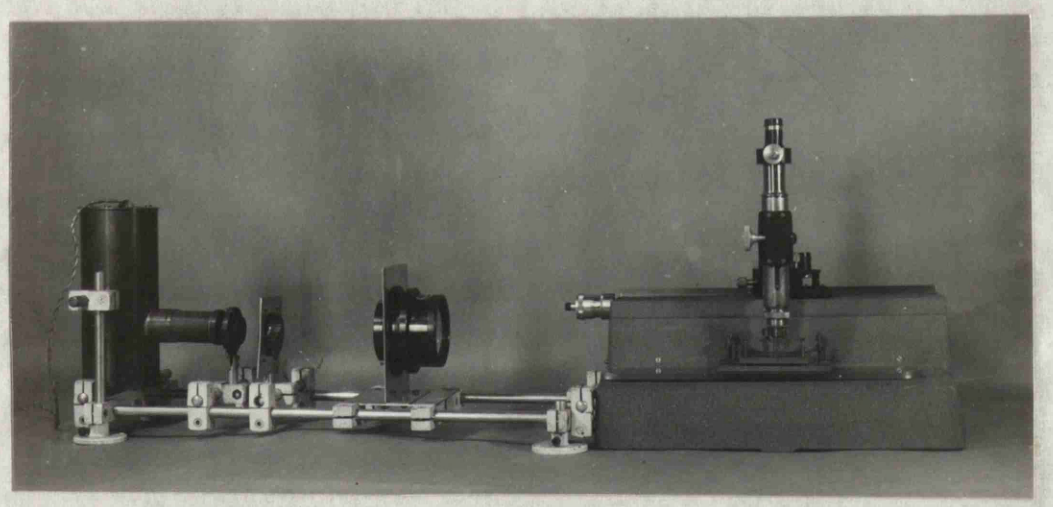


Plate 4.1. Optical arrangement for illuminating the interferometer and viewing the fringe system.

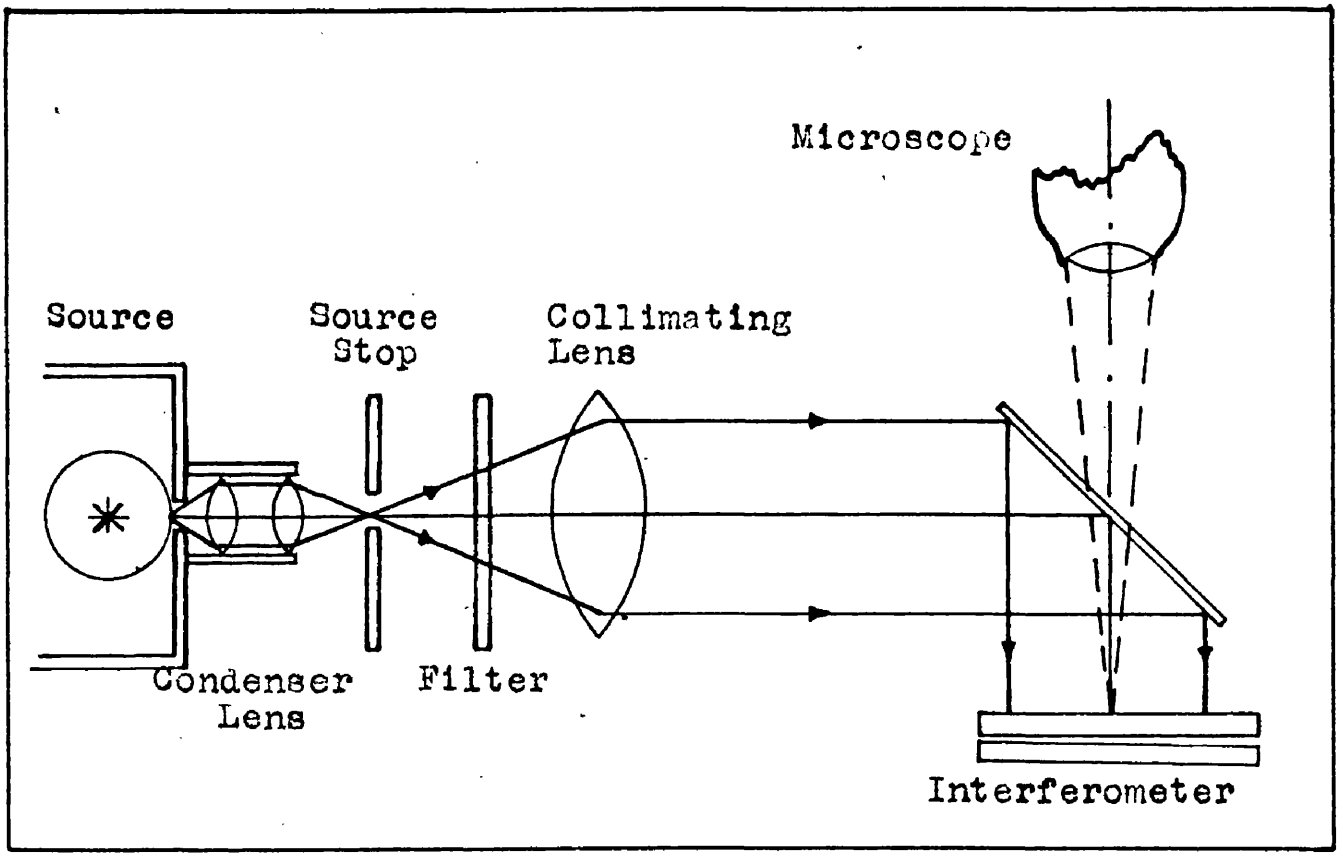


Figure 4.3. Diagram of the optical arrangement for viewing multiple-beam interference fringes of equal thickness in reflection.

the beams from the interferometer must be collected. All these factors were taken into account when setting up the above arrangement.

A typical reflection interferogram is shown in Plate 4.2. The displacement at the step edge indicates a film thickness of 550A. and the undulations of the microscope slide can be clearly seen.

The displacement of the fringes at the step and the fringe spacing were measured by a micrometer eyepiece which could be read with accuracy to 10 microns. With four to six fringes in the field of view the fringe spacing at the eyepiece was approximately 3,000 microns, that is, one angstrom per micron. Therefore, the accuracy of the thickness measurements was reasonably high. By measuring the displacement of a number of fringes across the step, approximately twelve and taking an average value, an accuracy of $\pm$ 10-20A could be achieved.

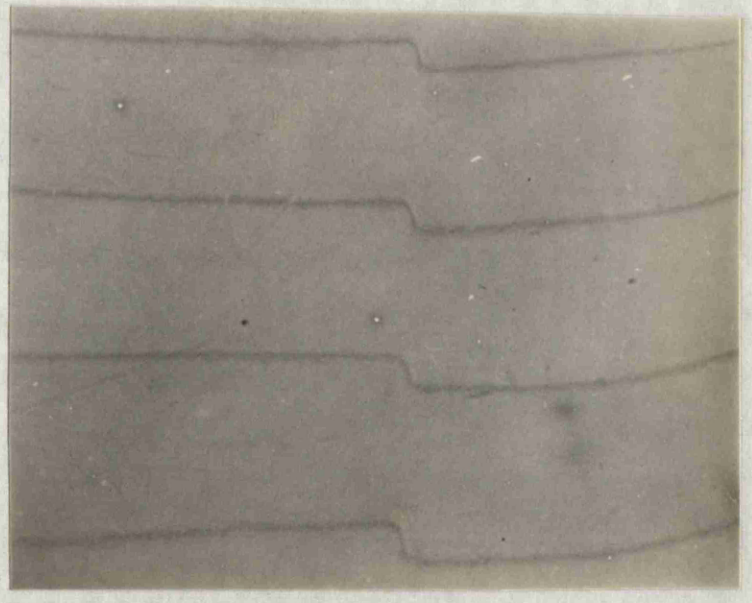


Plate 4.2. Typical reflection interferogram indicating a film thickness of 550A.

CHAPTER 5

THE MEASUREMENT OF ADHESION

1. Introduction

Heavens[21] has described a comparative method of measuring the adhesion of metal films deposited on surfaces. A loaded steel point of smooth contour was drawn across the film surface and the load required to remove the film completely from the surface was taken as a relative measure of the adhesion. The advantages of this method have been discussed already but, before this apparatus was used in the present investigation, it was felt that the mechanism of the method should be examined more closely. Though the load on the point required to remove the metal film completely from the surface may depend on the adhesion between the two media, this is not immediately obvious and other factors may influence the load; for example, the film thickness and the hardness of the film material. The magnitude of these factors must be examined before the apparatus can be used for a comprehensive investigation of the adhesion of thin films.

2. Apparatus

To obtain reliable and repeatable measurements with the apparatus particular attention must be paid to the steel point. The point must remain constant in its geometric dimensions and its physical properties, particularly hardness. It was found that gramophone needles served the purpose admirably. The needles used were H.M.V. 'Half-Tone' having a spherical tip of radius 0.0012-0.0018" and a diamond pyramid hardness of 800-850. These fine tolerances enabled the point to be changed at will while the dimensions and properties of the point remained reasonably constant.

The apparatus for the measurement of adhesion is shown in Plate 5.1. A rigid brass beam was pivoted about a horizontal stub axle fixed one quarter of the way along its length. The axle was mounted on a frictionless bearing, obtained from an old Attwood's machine. The steel point was fixed at the end of the long arm of the beam and a weight pan suspended half way between the point and the axle. The short arm of the beam carried two weights to act as counterbalances. One of the weights, a large brass block, moved along the beam and could be held at any point with a locking bolt. This weight gave a coarse balance. The final balance was made by a heavy brass disc mounted on a screwed rod at the end of the beam. By means of these

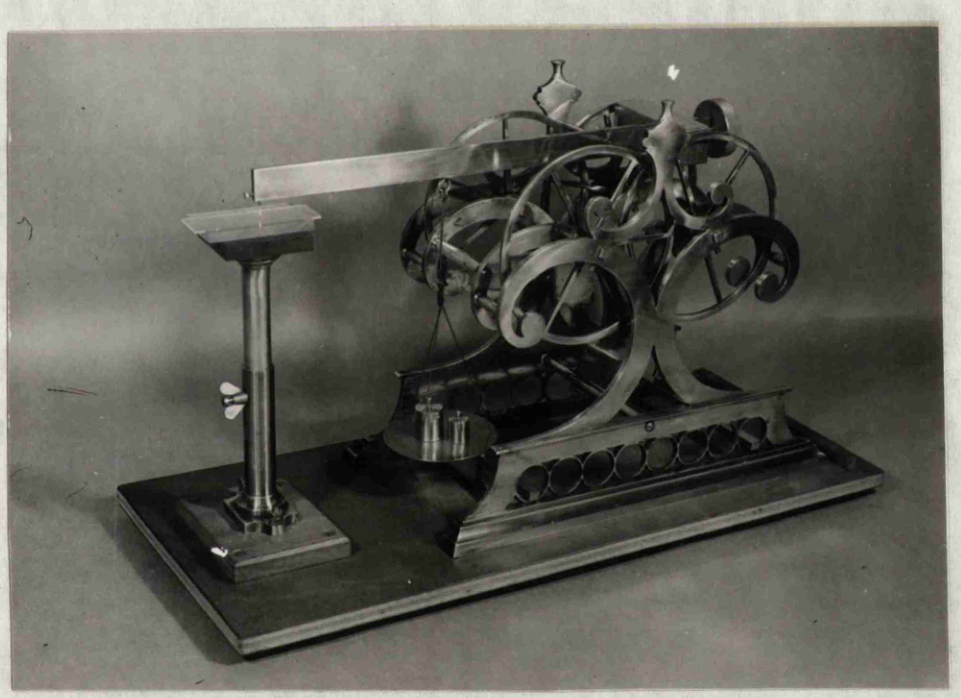


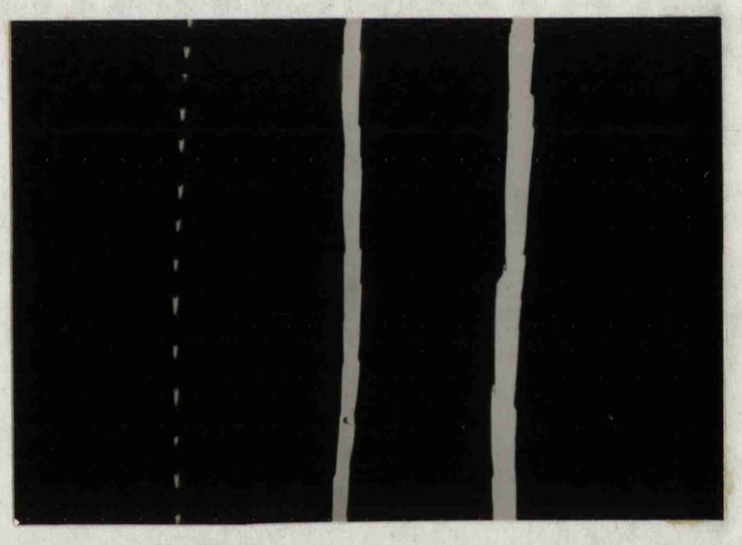
Plate 5.1. Apparatus for the measurement of adhesion.

weights the beam was balanced in the horizontal position. The specimen was raised on an adjustable table to the tip of the steel point. Thus the load on the point was initially zero.

3. Method of Measurement

A load was applied to the steel point by adding weights to the pan. The specimen was pushed slowly across the table and the scratch mark observed. The load was then adjusted until a clear scratch was obtained. The load at which this occurred was well defined; if the load was insufficient the steel point chattered over the surface giving a series of small scratches. As the load increased these scratches joined up and finally formed a clear scratch at the correct load. Increasing the load further only widened the scratch or gave it a jagged edge. Plate 5.2 shows a series of scratches: scratch (a) was made with insufficient load, scratch (b) was made at the correct load, and scratch (c) was made with an excess load.

The stage at which a clear scratch occurred could be judged very accurately by viewing the scratch marks in a low-power microscope by transmission. However, the attainment of very high accuracy was a laborious process and the slight variations between individual needles caused a small



(a) (b) (c)

Plate 5.2. Series of typical scratches made by the apparatus for the measurement of adhesion.

scatter in the final results. Since the loads required to give a clear scratch on a number of metal-substrate pairs varied from half a gram to greater than 500 grams, an accuracy of 5-10% was considered adequate.

4. Justification of Method

The question of whether this apparatus really gives a measure of the adhesion between a film and a surface must now be considered. The apparatus certainly reproduces one of the conditions of wear which films undergo in practical use and therefore gives a measure of the durability of the film. However, the durability depends on a number of factors; the thickness of the film, the hardness of the film material, the formation of a protective oxide coating on the surface of the film, and, of course, the adhesion between the film and the surface. The influence of each of these factors on the load required to give a clear scratch must therefore be determined.

The influence of film thickness was examined by depositing a film of varying thickness on a surface. Figure 5.1 shows how this was achieved. A very thin film of metal was deposited by evaporation over the whole surface of the substrate and, by rotating the specimen in the rotating mechanism described previously, sections were progressively

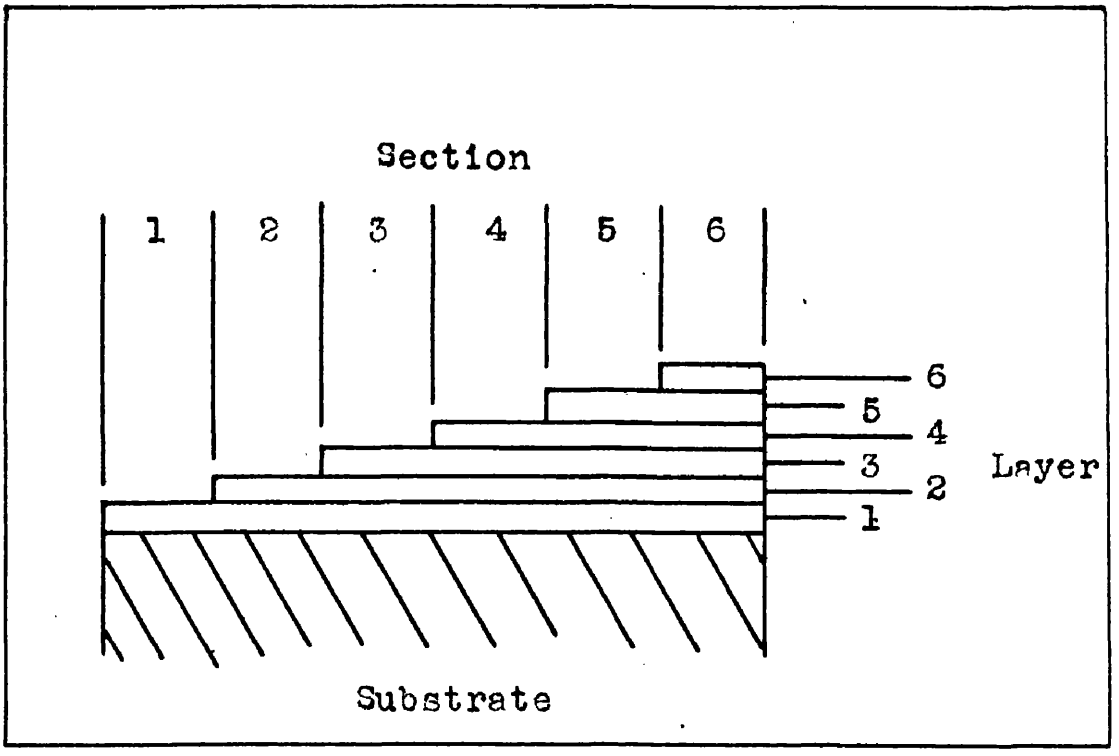


Figure 5.1. Deposition of six layers to give sections of varying film thickness.

screened from the vapour stream to give six sections of varying thickness on the substrate. Thus each section was built up from the same initial layer in contact with the substrate so that the adhesion forces in each case would be the same. Since the six layers were deposited continuously without a break in the vacuum, there should be no contaminating intermediate layers. The load required to give a clear scratch was measured for each of the six sections and the whole substrate was then coated with an opaque layer of silver and the thickness of each layer measured by multiple-beam interferometry. Several specimens were prepared in this manner and Figure 5.2 shows the variation of the load W against film thickness. It can be seen that in all cases the load reaches a constant value when a certain film thickness is attained. For films thinner than this critical thickness there is a variation of load with thickness. However, it would appear from Figure 5.2 that this is not a fault of the method but a property inherent in the films due to the process of film growth. It is well known that most thin films have an aggregated structure[41] and only become continuous above a certain thickness, this thickness being, to some extent, dependent upon the conditions of deposition. In depositing six layers, the film would build up gradually from an

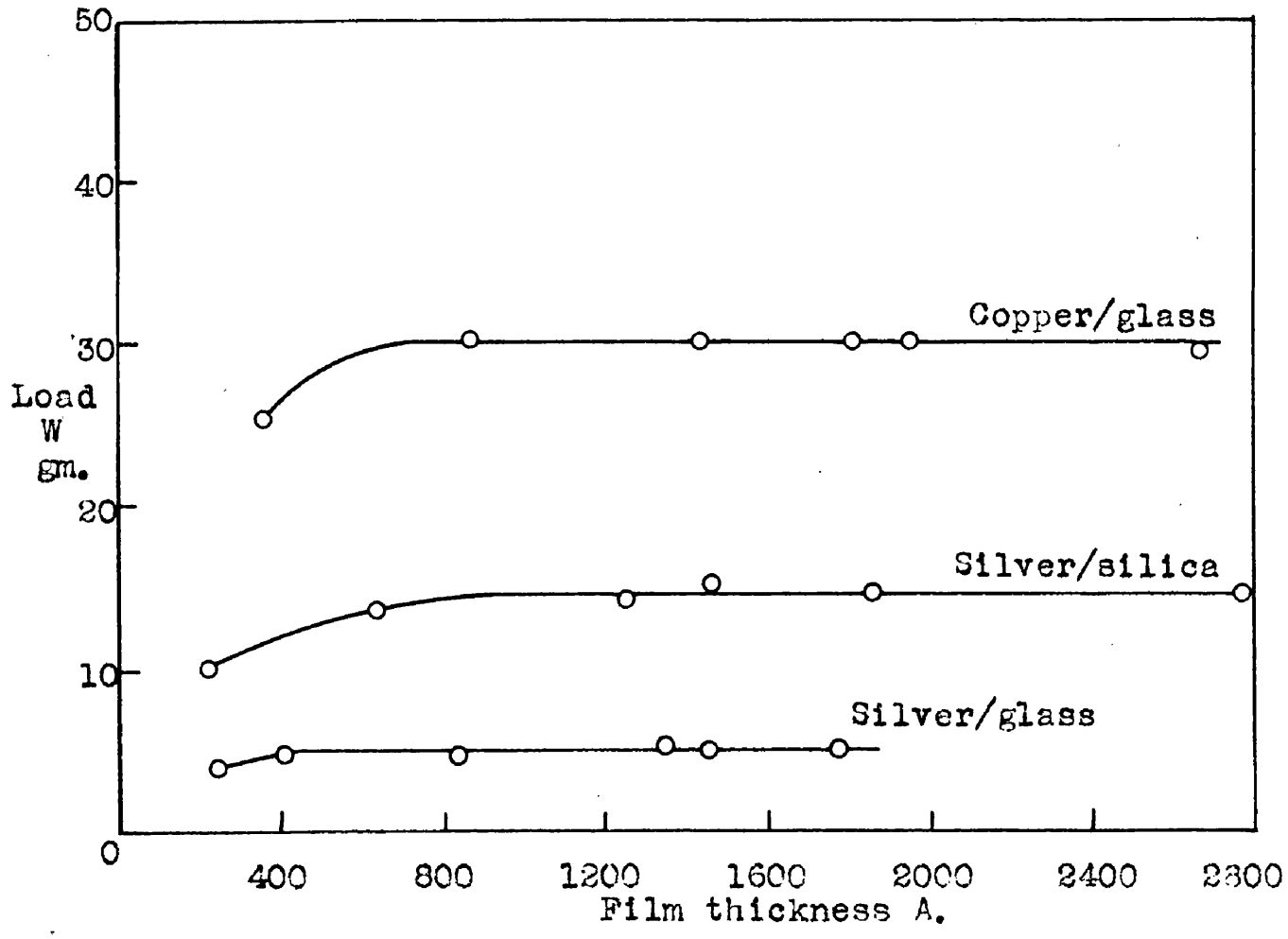


Figure 5.2. The load W required to remove a metal film of varying thickness from a surface.

aggregated to a continuous structure. Once the film was continuous there would be a continuous interface between it and the substrate and a certain load would be required to remove the film independent of its thickness. However, for aggregated films the interface would not be complete and therefore a smaller load would be required to remove the film.

The influence of the hardness of the film material and the formation of an oxide coating on the film surface on the load required to remove the film was examined in the following manner. A number of films of various metals were deposited on glass. The metals were selected to include noble metals on which an oxide layer would not form and several metals on which an oxide layer would readily form, in some cases providing a strong protective coating. The initial growth of the oxide layer is rapid and a thickness, only a little less than the final thickness, is reached in a matter of minutes[44]. Therefore, the films were removed from the vacuum chamber after deposition and allowed to stand in air for a short period of time. The load required to remove these films from the glass substrate was then determined. Table 5.1 shows the result of this investigation. The Mohs hardness for the metal and the metal oxide[45] is given together with the load required to

TABLE 5.1

Mohs hardness for some metals and their oxides and the load required to remove a film of the metal from glass

Metal	Hardness	Oxide	Hardness	Load gm.
Ag	2.5	-		5
Au	2.5	-		2
Pt	4.3	-		1
Sn	1.8	SnO_2	7.0	2
Mg	2.0	MgO	6.0	Non removable
Cu	2.5	Cu_2O	4.0	25
Zn	2.7	ZnO	4.0	3
Al	2.5	Al_2O_3	9.0	6

remove the film. It can be seen that there is no apparent connection between the load and the hardness of either the metal or the oxide.

5. Conclusions

It has therefore been shown that the load required to remove a film completely from a surface is not influenced by the hardness of the film material or the formation of an oxide coating on the film surface. Even the slight variation of load with film thickness at very small thicknesses can be explained in terms of film growth. Furthermore, when the same material was deposited on a number of different substrates it was found that the vertical loads required in measuring the adhesion by this method vary with the substrate material. Results obtained with silver on a number of different substrates are given in Table 5.2 where a wide variation can be seen. This suggests that the measurements depend upon the nature and properties of the interface between the deposited film and the substrate surface, but do not depend markedly on the thickness of the film or its bulk properties.

Table 5.2.

The load required to remove a silver film from the surfaces of various materials

Material	Vertical Load gm.
Silica	10
Glass	7
Perspex	100
Polystyrene	25
C.R.39	100
Xylonite	60
NaCl (100)	10
KBr (100)	9
KCl (100)	10

CHAPTER 6

CALIBRATION OF THE ADHESION MEASURING APPARATUS

1. Introduction

The relative adhesion of a metal film deposited on a surface has been measured by drawing a loaded spherical steel point across the film. If the mechanism of this action is examined, the factors involved are the forces acting on the point and the area of contact between the point and the surface, and it should be possible to estimate the force required to remove the film from the surface. There are two forces acting on the point, a vertical force due to the load and a horizontal force due to the action of drawing the loaded point across the film. Each of these forces must be examined together with the area of contact between the point and the surface.

2. Area of Contact

The dimension of the spherical tip of the gramophone needle (0.003 - 0.0045 cm.) in comparison with the thickness of the metal film (10^{-6} - 10^{-5} cm.) is such that the latter can be neglected and the area between the spherical

point and the substrate surface need only be considered.

In the ideal case, a flat surface is deformed by a hard sphere of radius r. This deformation is elastic and, according to Hertz's[45] classical equation, a load W gives an area of contact of radius 'a' where 'a' is given by the expression

$$a = 1.1 \left\{ \frac{Wgr}{2} \left(\frac{1}{E_1} + \frac{1}{E_2} \right) \right\}^{1/3}$$

and E_1 and E_2 are the Young's Moduli of the sphere and surface respectively. At this stage

$$a \propto W^{1/3}$$

As the load is increased a critical point is reached in the softer surface material when the elastic limit is exceeded. At this stage the mean pressure, p_m, over the area of contact is given by

$$p_m = 1.1\ Y \quad [47]$$

where Y is the yield strength of the softer material, or

$$p_m = 0.4 \times \text{Indentation Hardness} \quad [48]$$

This is the onset of plastic deformation. As the load is increased the mean pressure rises steadily until the whole of the material about the sphere is in a state of plasticity.

Once full plasticity is reached a further increase in W gives no change in the mean pressure, that is

$$a \propto W^{1/2}$$

and at this stage

$$p_m' = 3Y \quad 47$$

or

$$p_m' = \text{Indentation Hardness} \quad 48$$

The load required to cause the onset of plasticity is given by the Hertzian equation

$$W = \frac{13.1}{g} p_m^3 r^2 \left(\frac{1}{E_1} + \frac{1}{E_2}\right)^2$$

The case of a gramophone needle pressed on to a glass surface was considered. The needle has a hardness of approximately 800×10^8 dynes/cm.^{2}, while the indentation hardness for glass, measured by a Vickers Pyramid Hardness Testing Machine on an actual specimen, was found to be 400×10^8 dynes/cm.^{2}. Therefore, for a certain load on the needle plastic deformation would occur in the glass surface. Though the tip radius of the needle was given by the manufacturers as 0.003 - 0.0045 cm., it was found on examining a selection of the needles in a Vickers Projection Microscope that the tip radius was nearer to the minimum tolerance, that is, 0.003 cm. The values for the Young's Moduli for steel and glass were

taken as 20×10^{11} dynes/cm.^{2} and 7×10^{11} dynes/cm.^{2} respectively[49]. Substituting these values in the above equation, it was found that the onset of plasticity occurred at a load of 1.8 grams. For loads in excess of this value plastic flow occurred and, under these conditions, the area of contact could be calculated from

$$W = p'_m . A$$

where A is the area of contact.

The values of 'a', the radius of the area of contact, calculated for various loads W are graphed in Figure 6.1. Also shown in Figure 6.1 are some experimental values of 'a' obtained by measuring the track width of scratches made at different loads on a thin metal film deposited on glass. It can be seen that there is good agreement between the theoretical and experimental values of 'a'. The experimental values are somewhat higher and this is to be expected since some elastic deformation occurs around the contact area and the area is slightly greater than that predicted by the theory.

Further evidence of plastic deformation was given by an examination of the scratch contours using multiple-beam interferometry. Scratches were made at various loads on thin metal films deposited on glass and it was seen that the

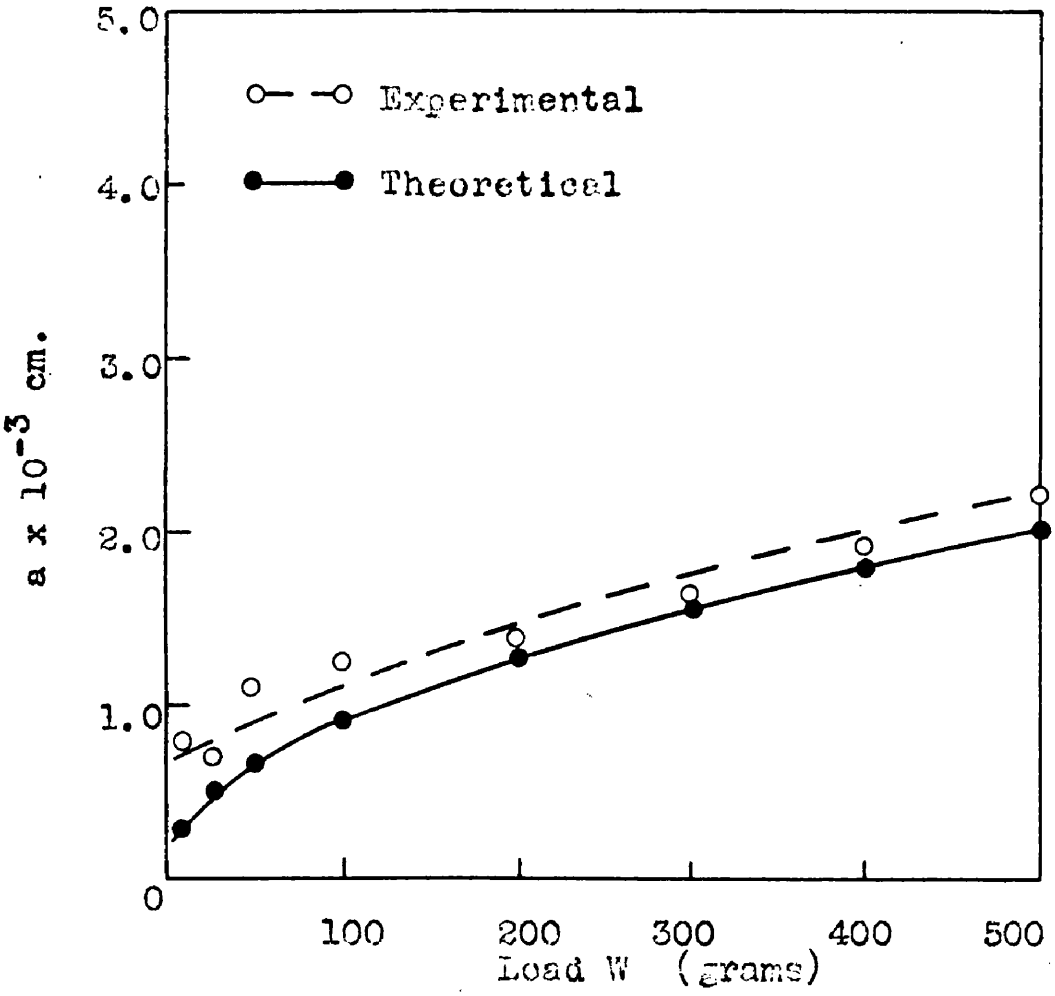


Figure 6.1. Theoretical and experimental values of the radius of the area of contact for various loads.

depth of the scratch increased with load and was always greater than the thickness of the metal film. This is shown in Table 6.1 from measurements made on a chromium film on glass.

Therefore, the area of contact between a spherical point and a plane surface could be calculated with reasonable accuracy, knowing the load on the point and the indentation hardness of the surface.

3. Horizontal Force

If the mechanism of removing the film by drawing the loaded spherical point across it is considered as a stripping action, then the horizontal force, F_h, acting on the point should be made up of three components. The first component is the ploughing force, P_1, due to the deformation of the substrate material. The second component is the force, F, due to the removal of the metal film from the substrate, that is, the force shearing the adhesion bonds between the film and the substrate. The third component is the ploughing force, P_2, required to push aside the sheared film.

According to Bowden and Tabor[50], the ploughing force, P_1, can be obtained from the expression

TABLE 6.1

The deformation of a glass surface due to increasing the load on the spherical point

Load gm.	Depth of Scratch A
10	330
20	425
50	510
100	575
200	847
300	935
400	1135
500	1585

Thickness of film 302A

$$P_1 = \frac{d^3}{12r} \cdot p'_m$$

where d is the track width, r is the radius of the spherical point, and p'_m is the indentation hardness of the substrate material.

The force, F, due to shearing the metal film from the substrate can be expressed in the form

$$F = f \cdot \frac{\pi d^2}{4}$$

where f is the shearing force per unit area between the film and the substrate.

The second ploughing component, P_2, is dependent on the thickness, t, of the metal film and the indentation hardness, p'_{m_1} of the film material, so that,

$$P_2 = d.t.p'_{m_1}$$

The value of f for a metal-substrate pair is not easy to estimate but the order of magnitude can be obtained by a method similar to that used by Frenkel[51] in viscosity problems.

The simplest case is taken where shearing occurs between the bonds of two different media in which the atoms

are in layers, as in Figure 6.2. A is a layer of atoms of the metal film and B is a layer of atoms of the substrate material, the two layers being a distance x_1 apart. A force per unit area, f, is applied so that one layer is displaced with respect to the other. The movement of an atom of layer A from one equilibrium position to the next in layer B may be considered as equivalent to the passage of the atom over a potential barrier. Let x be the distance between two such positions in the direction of motion, x_3 the distance between neighbouring atoms in the same direction, and x_2 the distance between two adjacent atoms in the moving layer. If the potential barrier is assumed to be symmetrical then the distance between the equilibrium position and the top of the barrier is $x/2$. The applied force acting on an atom in layer A in the direction of motion is fx_2x_3 and the energy the atom acquires when it reaches the top of the potential barrier is $\frac{1}{2}fxx_2x_3$. Figure 6.3 shows the potential barrier and the way in which the applied shearing force reduces the height of the energy barrier by $\frac{1}{2}fxx_2x_3$ in the forward direction and raises it by the same amount in the opposite direction. If the height E is taken as a measure of the adhesive energy between an atom of layer A and the layer of substrate atoms B, then the expression

$$E = \tfrac{1}{2}fxx_2x_3$$

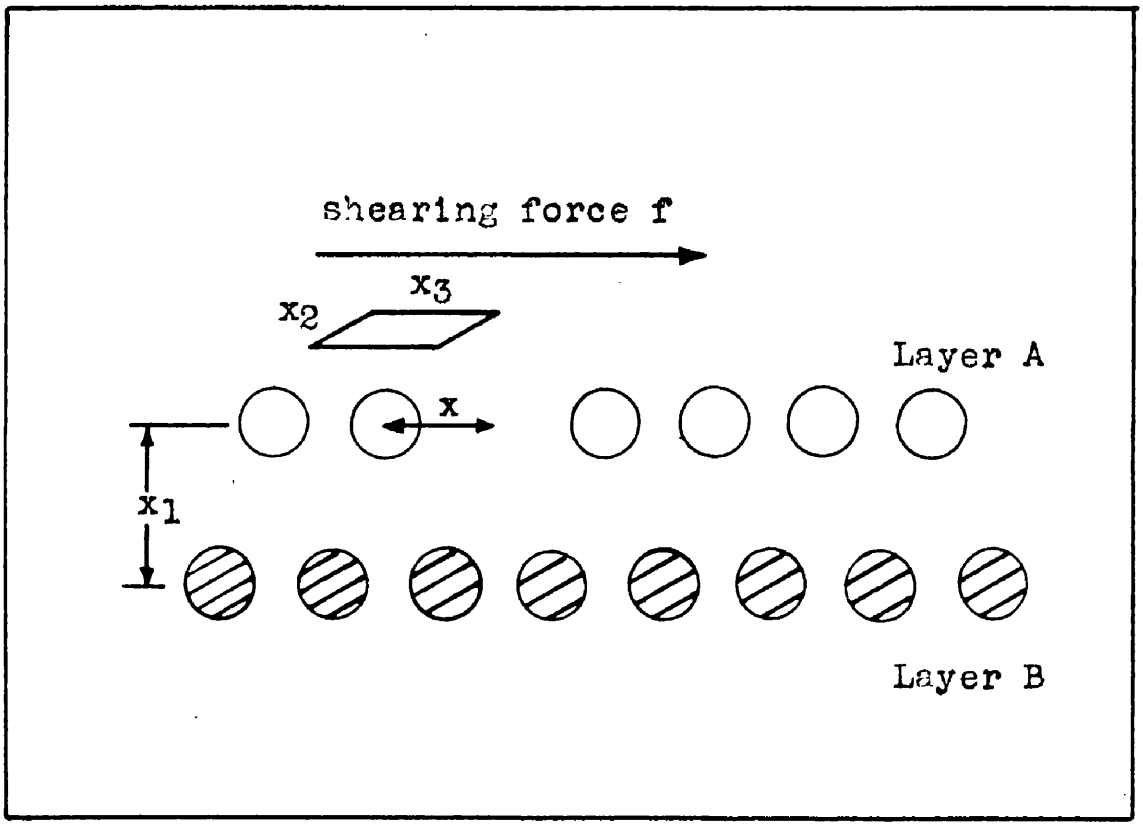


Figure 6.2. Displacement between two layers of atoms due to a shearing force.

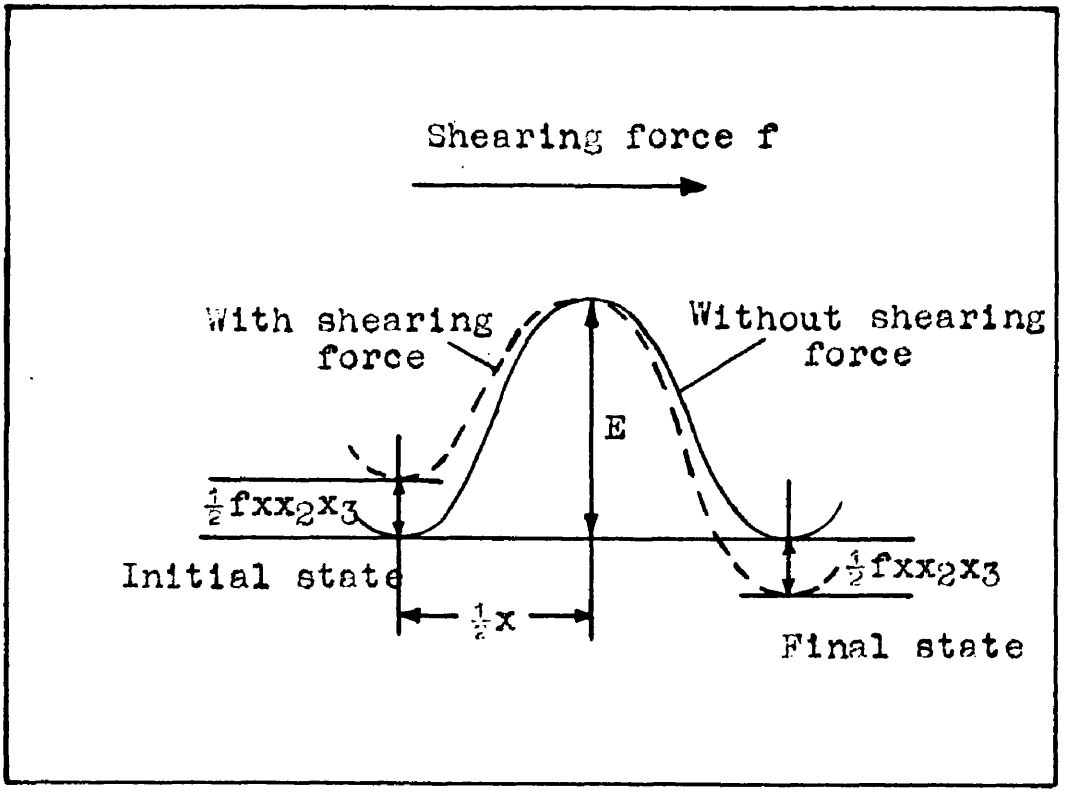


Figure 6.3. Potential energy barrier, with and without shearing force.

gives the order of magnitude for the value of the force which will shear an atom of layer A from the layer B.

The horizontal force, F_h, acting on the spherical point when a metal film is removed from a substrate can now be written in the form

$$F_h = \frac{d^3}{12r} \cdot p'_m + \frac{E}{\frac{1}{2}xx_2x_3} \cdot \frac{\pi d^2}{4} + d.t.p'_{m_1}$$

Let us consider a metal film, 500A thick, bound to a glass surface by van der Waals' forces and assume a value for the adhesive energy between the two media of 3.0 K.cal./mole. Let us also assume values for x, x_2 and x_3 of 3A, and for p'_m and p'_{m_1} of 10^{10} dynes/cm.^{2} and 10^9 dynes/cm.^{2} respectively. Finally, let the load required on the point to remove the film be such that the track width is 0.002 cm. Thus f, the shearing force/unit area, is 15×10^9 dynes/cm.^{2}. If these values are now substituted in the above equation, the horizontal force should be

$$F_h = (2.2 + 46.5 + 10) \times 10^3 \text{ dynes.}$$

This calculation, giving the relative orders of magnitude of the various components making up the horizontal force, was checked experimentally as follows.

A second beam was constructed for the adhesion measuring apparatus being almost identical to the first beam but having a length of springy material inserted between the weight pan and the steel point. When the point was drawn across the film surface under a given load the horizontal force on the point caused the flexible beam to deflect. The deflection was measured very simply by means of a pointer, attached to the beam, moving over a scale and the deflection was calibrated.

The adhesion of a number of metals on glass and silica was studied in this manner. To examine the effect of thickness, the films were deposited to give six sections of varying thickness on the substrate by the method described in Chapter 5. With the rigid beam on the apparatus, the loads required to remove the various thicknesses of film from the substrate were found. Then, with the flexible beam in position and the correct load in the weight pan, the horizontal force, F_h, involved in removing the film was measured in each case. The ploughing component, P_1, of this force due to the deformation of the substrate was measured by repeating the test on an uncoated substrate, which had been cleaned in the usual manner including exposure to a glow discharge. By subtraction, the component of the horizontal force due to shearing the metal film from the

substrate and pushing it aside was obtained, that is, $F + P_2$. Table 6.2 shows some of the results and it can be seen that the horizontal forces are very much lower than expected. The magnitude of the forces and their increase with film thickness suggests that the residual horizontal force was P_2, and that the motion of the point across the film surface was only pushing aside the film material, the adhesion bonds between the film and the substrate having already been broken.

In the previous chapter it was shown that the vertical load required to remove a metal film completely from a substrate was independent of film thickness (for thicknesses greater than 500A), independent of the hardness of the metal and the formation of a protective coating, but dependent upon the film material and the nature of the substrate. On the other hand, after allowances have been made for any ploughing effects that might be present, the horizontal force does not seem adequate to shear the adhesion bonds between the film and the substrate. This would suggest that the adhesion bonds are sheared as a result of the deformation of the surface produced by the vertical load.

4. Vertical Load

It has been shown that when a loaded spherical point rests on a surface deformation of the surface occurs. If a metal film has been deposited on the surface then it

TABLE 6.2

Horizontal force required to shear a metal film from a surface

Film Thickness A	Vertical Load $\times 10^3$ dynes	Horizontal Force F_h $\times 10^3$ dynes	Ploughing Component P_1 $\times 10^3$ dynes	$(F + P_2) = (F_h - P_1)$ $\times 10^3$ dynes
Silver/Glass				
105	3	0.3	0.2	0.1
265	4	0.9	0.8	0.1
457	5	1.1	1.0	0.2
770	5	1.4	1.0	0.4
1038	5	1.5	1.0	0,5
Copper/Glass				
359	25	6.0	5.5	0.5
871	30	7.5	6.5	1.0
1336	30	8.3	6.5	1.8
1672	30	9.0	6.5	2.5
1935	30	10.0	6.5	3.5
2580	30	11.0	6.5	4.5
Silver/Silica				
225	10	2.5	2.3	0.2
629	13	3.5	3.0	0.5
1258	14	4.0	3.2	0.8
1473	15	5.0	3.5	1.5
1857	15	5.5	3.5	2.0
2660	15	6.3	3.5	2.8

will also be deformed to contour the shape of the indentation, as shown in Figure 6.4. This would cause stretching of the film and a shearing force to be set up at the interface between the film and the substrate. This shearing force would have a maximum value at the lip of the indentation and the tensile forces in the film would be small in comparison. Rupture of the film around the area of contact would readily occur. As the load was increased so the shearing force would increase until it reached a value at which the adhesion bonds between the film and the substrate would be broken at the lip. Once this occurred the shearing of the film would readily extend over the whole indentation and the horizontal motion of the point would push the sheared metal aside.

Figure 6.5 shows in more detail the forces acting on the spherical point. W is the load on the point of radius r, F is the shearing force per unit area due to the deformation of the substrate, and 'a' is the half track width. P is a force acting against the deformation and, when this deformation is plastic, P is similar to a uniform hydrostatic pressure acting normal to the surface of the indentation and, therefore, can be taken as the indentation hardness of the substrate material. From the triangle of forces, ABC, shown in Figure 6.5

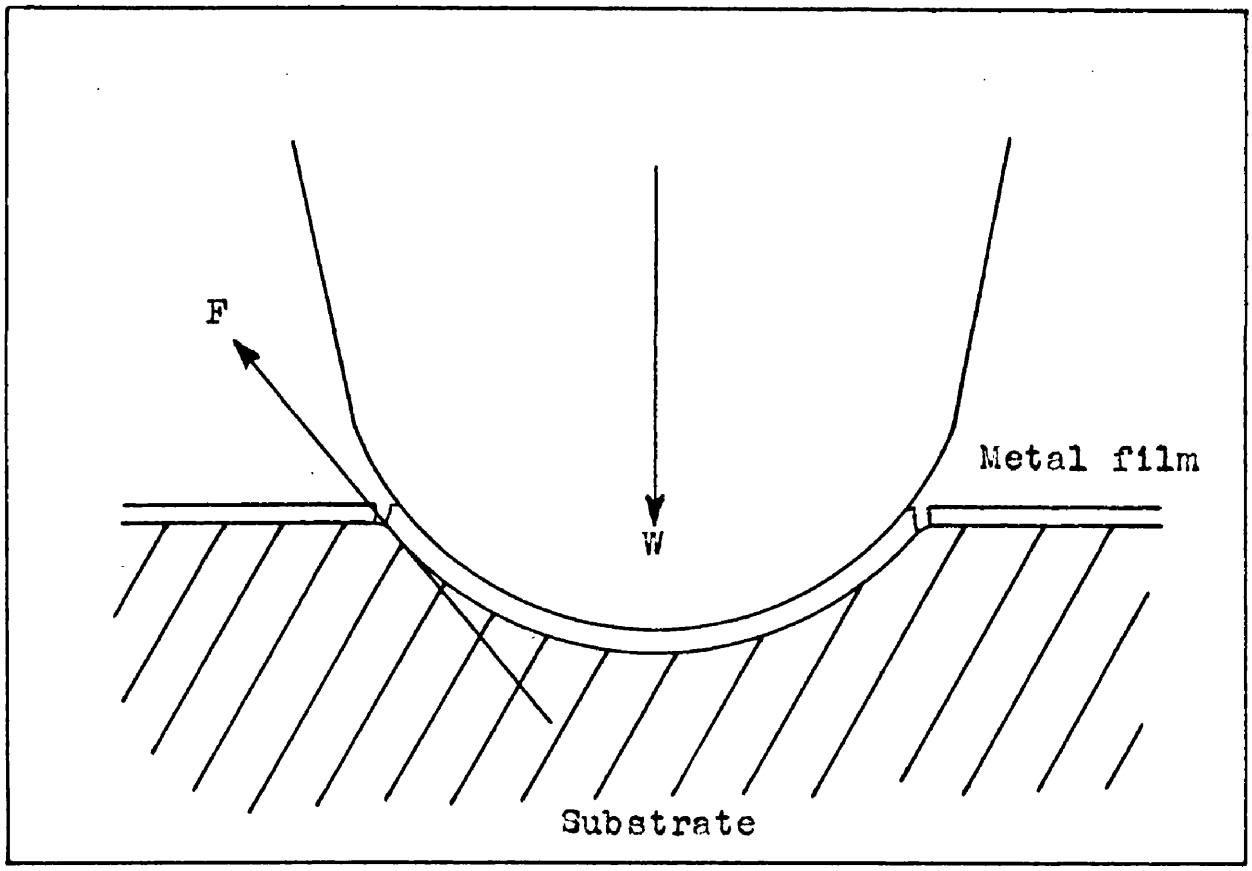


Figure 6.4. Shearing force due to the deformation of the substrate.

$$F = P.\tan\theta$$

$$= \frac{a}{\sqrt{r^2 - a^2}} . P$$

It has been shown earlier in this chapter that

$$a = \sqrt{\frac{W}{\pi P}}$$

Table 6.3 shows the values of F for various loads on a point of radius 0.003 cm. pressing on a glass surface. It can be seen that the values are of the right order of magnitude when compared with the approximate value of 15×10^9 dynes/cm.^{2} for the force required to overcome van der Waals' forces between a metal film and a glass surface as calculated earlier.

If the theory is correct then the geometry of Figure 6.5 indicates that, for the shearing force, F, to remain constant, an increase in r will require a corresponding increase in the vertical load. To give the variation of radius, ball bearings of diameters 1/32" and 1/16" were mounted on steel pegs. These, together with the gramophone needles, gave a series of radii of 0.003, 0.040 and 0.080 cm. Adhesion tests were carried out on a number of metal films deposited on glass and Table 6.4 shows the result of one such test. As the radius of the spherical point was increased

TABLE 6.3

The shearing force, F, for various loads on glass

Load gm.	Shearing force, F x 10^8 dynes/cm.^{2}
5	30.0
10	41.7
25	66.6
50	95.0
100	133.5
250	212.0
500	298.0

TABLE 6.4

Variation of the radius of the spherical point

Tip radius cm.	Load cm.	a (exper.) cm.	a (theor.) cm.	F dynes/cm.^{2}
0.003	3	0.0008	0.0002	21×10^8
0.040	300	0.003	0.002	20×10^8
0.080	1000	0.005	0.003	15×10^8

so the load required to remove the film increased to give a reasonably constant value for the shearing force, F.

In accordance with the theory, when different substrate materials are used and adhesions have to be compared, the indentation hardness of the material must be considered, since the shearing force is dependent on both the vertical load and the hardness of the substrate. This is shown in Table 6.5 where the vertical loads required to remove a silver film from a number of materials are tabulated. It would appear from the vertical load alone that silver has the greatest adhesion to plastics and a poorer adhesion to glass-like materials and crystal faces. However, the true picture is obtained when the indentation hardness of the material is taken into account and the shearing force, F, required to remove the film is calculated, as in column 4. It can then be seen that silver has the strongest adhesion to glass and silica, a weaker adhesion to the plastics, and a poor adhesion to crystal faces.

5. Calibration of the Apparatus

It appears then that the mechanism by which a film is removed from a substrate surface is one in which the film is first sheared from the surface by the vertical load on the spherical point and then pushed aside by the horizontal

TABLE 6.5

Adhesion of a silver film to the surfaces of various materials

Material	V.H.N.	Vertical load gm.	$F \times 10^8$ dynes/cm.^{2}
Silica	496	10	42
Glass	400	7	32
Perspex	25.0	100	30
Polystyrene	22.0	25	14
C.R.39	18.0	100	24
Xylonite	14.5	60	16
NaCl (100)	18.6	10	8.1
KBr (100)	9.0	9	5.0
KCl (100)	8.0	10	5.3

motion of the point. The shearing force which removes the film can be calculated from the value of the vertical load required to give a clear scratch, the radius of the spherical point, and the indentation hardness of the surface material.

The indentation hardness of a number of substrate materials was measured by the Vickers Pyramid Hardness Testing Machine and, knowing the elastic modulus of each material, the onset of plasticity was calculated for each material. From Table 6.6 it can be seen that, for a tip radius of 0.003 cm., plasticity occurs at very light loads, even for the hardest material. Thus calibration curves can be drawn for a given tip radius so that the shearing force at the interface is known for any load greater than that which causes the onset of plasticity. Figure 6.6 gives such calibration curves for the apparatus using a tip radius of 0.003 cm. and a number of indentation hardnesses.

6. Conclusions

The apparatus described can be used either as a comparative measure of adhesion for films on the same substrate by simply comparing vertical loads or for an absolute measurement of adhesion. From the calibration curves, it can be seen that adhesion measurements will be more accurate

TABLE 6.6

THE ONSET OF PLASTICITY FOR VARIOUS MATERIALS

Material	E x 10^{11} dynes/cm.^{2}	V.H.N. x 10^8 dynes/cm.^{2}	Onset of Plasticity grams.
Silica	8 †	496	2.8
Glass	7 †	400	2.0
Perspex	0.15 - 1.0 †	25.0	0.005
Polystyrene	"	22.0	0.005
C.R. 39	"	18.0	0.002
Xylonite	"	14.5	0.001
NaCℓ (100)	2.5 *	18.6	0.001
KBr (100)	1.6 *	9.0	0.0001
KCℓ (100)	1.7 *	8.0	0.0001

† Kaye and Laby[52]

* Kittel[53]

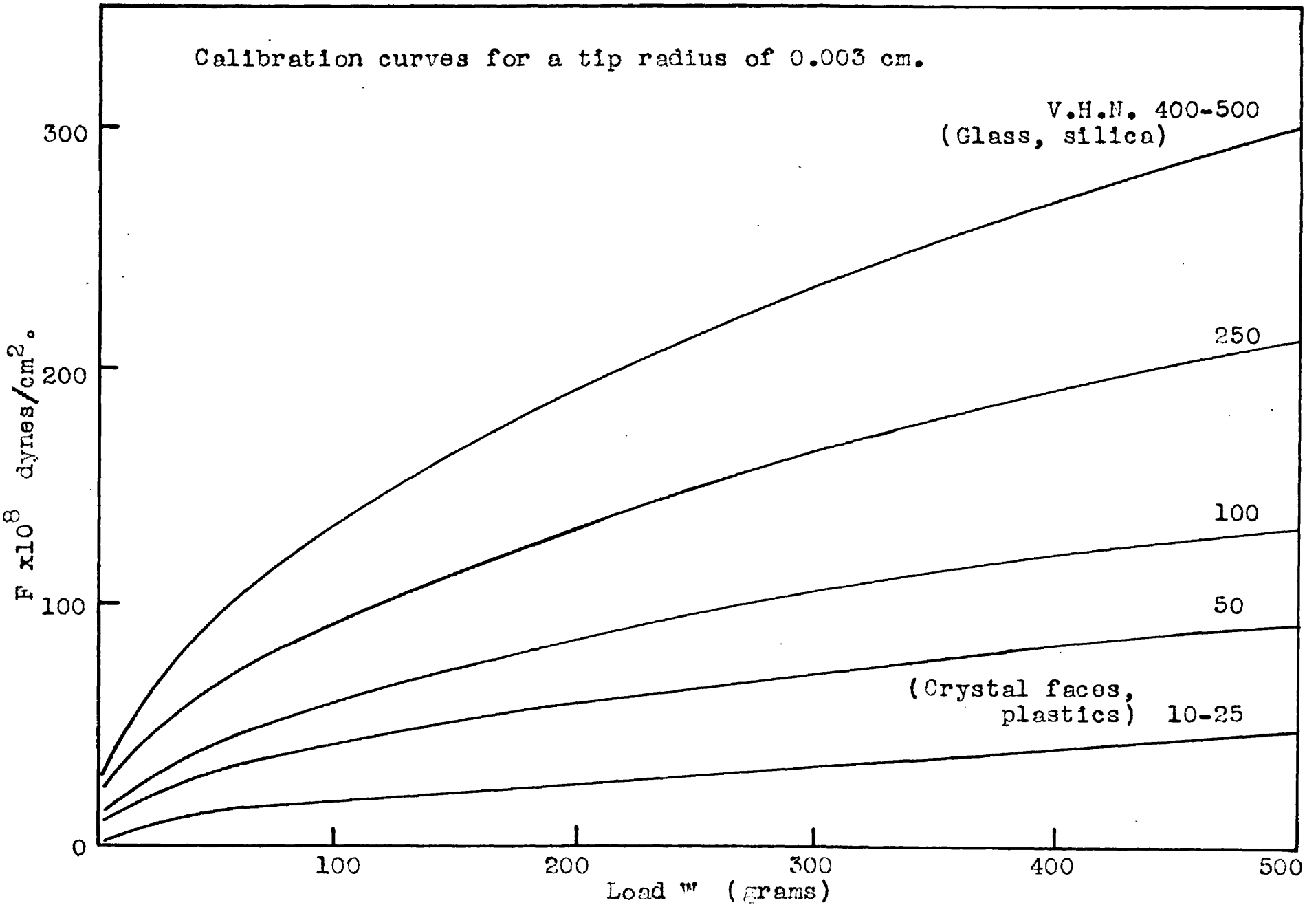


Figure 6.6. Calibration curves for various indentation hardnesses.

on hard substrates where the shearing force varies more rapidly with vertical load. Accurate use of this apparatus will be limited to absorbing films on transparent substrates since the scratches should be viewed in a low-powered microscope using transmitted light.

CHAPTER 7

THE ADHESION OF THIN METALLIC FILMS TO GLASS

1. Introduction

The metals examined in this investigation were Au, Ag, Al, Cr, Pb, Ni, Cu, Ca, Mg, Mn, Zn, Cd, Mo, Sn, Fe, Ti and Zr. Thin films of these metals were deposited by evaporation on to high quality soda-silica microscope slides. A number of specimens of each metal having a range of thickness were deposited at varying rates. After deposition of the film, the specimen was removed from the vacuum chamber and the adhesion measured immediately and the time between deposition and the first adhesion measurement was approximately four minutes. Since all the measurements were made on a glass surface, the figures given for the adhesion are the vertical loads required to remove the films and not the actual shearing forces developed. The adhesion was measured at intervals over a period of 600 hours in order to study any ageing effects which might occur, the specimens being kept at room temperature in a dessicator between measurements.

2. Results

The variation of adhesion with time for a selection of metal specimens are shown in Figures 7.1 - 7.14 at the end of the chapter and the adhesion results for all the metals examined are described below.

Gold (Fig. 7.1). Gold films were deposited at rates varying between 1-14 A/sec. and had a thickness range of 100-1300A. The adhesion of all the gold films examined was poor (2 gm.) and there was no variation of adhesion over the 600 hour ageing period.

Silver (Fig. 7.2). Silver films having a thickness range of 100-1600A were deposited at rates varying from 8-90 A/sec. For all the films examined the initial adhesion was poor (5 gm.) but in each case there was a slight increase of adhesion over the 600 hour time period.

Lead (Fig. 7.3). The adhesion of all the lead films examined was extremely poor ($\frac{3}{4}$ gm.) and there was no variation of adhesion with time. The thickness range for the lead films was 250-1200A and the rates of deposition were in the range of 5-40 A/sec.

Aluminium (Fig. 7.4). Aluminium films having a range of thicknesses between 60-1300A were deposited at rates varying

from 2-70 A/sec. In all cases the initial adhesion was poor (7 gm.) but there was a slight increase until, between 150 and 250 hours, a more rapid increase in adhesion occurred. At 300-500 hours an approximately constant value of 60-80 grams was reached.

Films of zinc and cadmium do not readily condense on glass at room temperature unless the vapour intensity is high or the substrate is precoated with atoms of a low vapour pressure metal to act as nuclei for condensation. Films of both metals were deposited on glass at room temperature without precoating the substrate.

Zinc (Fig. 7.5). The thickness range of zinc films examined was 130-400A and the rate of deposition ranged from 7-14 A/sec. The initial adhesion of the zinc films was poor (3 gm.) but there was a steady increase over the 600 hour time period to a final value of 8 grams.

Cadmium (Fig. 7.6). Cadmium films of thicknesses 175-790A, deposited at rates from 12-23 A/sec., were examined. Thick films had a milky white appearance which suggested a highly aggregated structure. The adhesion of all the cadmium films examined was poor (7 gm.) to begin with but there was a rapid increase to a value of 15-20 grams within 100 hours. The adhesion remained constant at this value for the rest of

the 600 hour time period.

Tin (Fig. 7.7). Tin films also had this milky white appearance at greater film thicknesses. The range of thicknesses examined was 250-1080A and the rate of deposition ranged from 3-12 A/sec. The adhesion was initially poor (2 gm.) and dropped to a smaller value ($\frac{1}{2}$ gm.) in a very short time, at which it remained for the rest of the time period.

Copper (Fig. 7.8). Copper films were deposited at rates from $4\frac{1}{2}$-20 A/sec. and covered a range of thicknesses between 130-500A. The adhesion remained constant over 600 hours at a value of 25-30 grams. However, in several cases, the initial adhesion was poor (10 grams) but rapidly rose to a constant value of 25-30 gm.

Manganese (Fig. 7.9). Manganese films, with thicknesses between 225-1500A, were deposited at rates of 6-40 A/sec., and all showed a steady rise in adhesion with time. The adhesion increased slowly from an initial value of 10 grams to about 50-100 grams in 200 hours; the increase then became more rapid, reaching a final value of 300-500 grams.

Nickel (Fig. 7.10). Unfortunately, nickel alloys with the filament material causing the filament to burn out rapidly.

Therefore, the deposition of thick films greater than 300A was found to be well nigh impossible. The thicknesses of the films examined ranged from 100-300A and were deposited at rates from 4-22 A/sec. All these films had a poor adhesion initially (10 gm.) but the adhesion increased steadily with time to a final value of 150-300 gm.

Iron (Fig. 7.11). Iron films, deposited at rates of 8-10 A/sec. and having a thickness range of 230-650A, adhered strongly to glass, the initial adhesion being 50-100 grams. Even so, there was a rapid rise in adhesion and after a short time the films could not be removed cleanly from the substrate. At loads greater than 500 grams the glass substrate cracked though the iron films still adhered and could not be completely removed. In this case, the adhesion was taken as the load which left the minimum amount of metal in the scratch. As the broken line indicates in the adhesion curve, this occurred at loads of 200-400 grams after a short time, though the adhesion soon increased to greater than 500 grams, that is, even at this maximum load, there was still a large amount of metal left in the scratch.

Chromium (Fig. 7.12). The adhesion of the chromium films examined was very similar to that of iron, the initial adhesion being 100-150 grams but soon rising to greater than

500 grams. The thickness range for these films was 150-1150A and they were deposited at rates of 1-6 A/sec.

Molybdenum (Fig. 7.13). Only very thin films of molybdenum were obtained. The initial adhesion of these films was poor (5 gm.) but there was a very rapid increase to an adhesion greater than 500 grams.

Titanium (Fig. 7.14). Only thin films of titanium were obtained, due to alloying of the metal with the source material. The initial adhesion of these thin films was of the order of 5 grams but there was a steady increase until, after 250 hours, the adhesion was greater than 500 grams.

Zirconium. For reasons similar to those in the case of titanium, only thin films of zirconium were deposited. In this case, however, the initial adhesion of the zirconium films was very high (100-300 gm.) and even then the film was not completely removed. The films were completely non-removable after 24 hours.

Magnesium. Magnesium films, having a thickness range of 120-450A, were deposited at rates varying from 9-13 A/sec. The thick films had the milky white appearance previously mentioned though, in this case, it may be due to the formation of white MgO. Though, initially, some of the

films examined could be removed from the substrate, the adhesion increased very rapidly so that all films were non-removable in a few hours.

Calcium. Adhesion measurements on calcium films were unobtainable since all the films deposited seemed to disappear, due to either re-evaporation or oxidation to a transparent layer. To examine this phenomenon, part of a freshly deposited calcium film was covered by an opaque silver film for a thickness measurement. The calcium film was then allowed to age and where not covered by silver seemed to disappear. A second silver film was deposited over the aged area of the calcium film, the thickness of which was then measured. The results of the two thickness measurements showed that complete oxidation of the aged calcium film had occurred, the thickness of the fresh deposit being 114A compared with 184A for the aged area.

3. Discussion

Levinstein[5] has suggested that the structure of a metal film can be correlated to the melting point of the metal from which it is deposited. As mentioned in Chapter 1, the structure must also be related to the adhesion forces acting between the condensing metal atoms and the

substrate surface so that films formed from high melting point metals which have a continuous structure should have a high adhesion to the substrate. Table 7.1 shows the metals examined in the present investigation in order of their melting points together with the initial and final values of adhesion. The high melting point metals do appear to have higher values of adhesion. Other physical properties are also noted such as the radius of the univalent ion and the van der Waals' adhesive energy between the metal and the glass surface (calculated after the method described in Chapter 2). Bateson[14] suggested that the adhesion of metals to glass was greater for metals having univalent cations of small radius but, by comparing columns 4 and 5, it can be seen that this suggestion is not confirmed by the results of this investigation. Similarly, by comparing columns 4 and 6, it can readily be seen that the magnitude and range of the adhesion of these metal films to glass and the ageing effects observed cannot be accounted for in terms of van der Waals' forces alone but must be attributed to some stronger force or to the formation of a chemical bond.

Williams and Backus[2] have given some results for the adhesion of metal films to glass. Unfortunately, the experimental conditions were not given and it must be assumed

TABLE 7.1

The adhesion of metal films to glass

Metal	M.P. °C	Adhesion gm. Init.	Final	Ionic Rad. A.	van der Waals' adhesive energy K.cal./mole
Mo	2620	5	> 500	0.93	2.5
Cr	1800	100	> 500	0.81	1.5
Ti	1800	5	> 500	0.96	2.4
Zr	1600	200	> 500	1.09	1.9
Fe	1539	100	> 500	-	2.8
Ni	1452	10	200	-	3.3
Mn	1460	10	400	0.75	1.2
Cu	1083	5-30	30	0.96	3.0
Au	1063	2	2	1.37	2.1
Ag	916	6	8	1.26	2.6
Al	660	7	60	0.72	3.4
Mg	651		> 500	0.82	1.6
Zn	419	3	8	0.88	2.3
Pb	327	$\frac{3}{4}$	$\frac{3}{4}$	1.06	2.3
Cd	321	5	15	1.14	2.0
Sn	232	2	$\frac{1}{2}$	0.96	1.2

that the adhesion measurements were made on freshly deposited films. They observed the stripping action of collodion pressed on to the surface of the metal films but, in any case, only a rough estimate of adhesion could be obtained. All that was observed was whether the films were readily removed from the glass substrate, occasionally removed, or were non-removable. Their results are compared with the results of the present investigation in Table 7.2 and it can be seen that there is fair agreement except for lead. Williams and Backus pointed out that the metals which were non-removable also formed oxides readily.

Weyl[12] has suggested that the adhesion of a metal film to glass could be due to the continuation of the glass structure by an intermediate oxide layer which would act as a bridge between the incompatible structures of the metal film and the glass surface. The way in which this oxide bond between the metal film and the glass surface could be formed has been described by Bateson[14], who considered that a freshly created glass surface was extremely reactive due to centres of incomplete co-ordination of the silicon ions and centres with an excess of oxygen ions. The free valency forces of the silicon ions have to be satisfied and this could be achieved by trapping water molecules from the surrounding atmosphere. In this way a neutral layer of

TABLE 7.2

COMPARISON OF THE RESULTS OF WILLIAMS AND BACKUS WITH THOSE OF THE PRESENT INVESTIGATION

Williams and Backus

Readily Removed	Occasionally	Non-Removable
Rh, Pd, Pt, Au	Ni, Cu, Ag, In	Be, Al, Cr, Mn, W, Pb, Ur

Present Investigation

Adhesion (grams)							
1	1-4	4-9	10-20	20-50	50-150	150-500	>500
Initial Adhesion							
Pb	Au Zn Sn	Ag Al Cd Ti Cu Mo	Ni Mn	Cu	Fe Cr		Zr Mg
Final Adhesion							
Pb Sn	Au	Ag Zn	Cd	Cu	Al	Mn Ni	Mo Cr Ti Zr Fe Mg

OH groups could be formed on the glass surface. Bateson suggested that the impinging metal atoms would react with these groups to form an oxide bond with the glass surface, the strength of the bond depending upon the affinity of the metal for oxygen.

In agreement with this suggestion, Table 7.1 shows that the noble metals, gold and silver, have a poor adhesion to glass. These metals do not easily combine with oxygen and would not therefore react readily with the OH groups on the glass surface to form an oxide bond. The adhesion of these metals to glass would probably be due to van der Waals' forces. On the other hand, magnesium, zirconium, and molybdenum become non-removable from a glass surface almost immediately after deposition. These metals have a great affinity for oxygen and could combine readily with the oxygen of the OH groups on the glass surface. It appears then that the affinity of a metal for oxygen does affect the adhesion of a metal film to a glass surface. However, the oxygen of the neutral OH groups is bonded on one side to the silicon ion in the glass surface and, on the other, to the hydrogen atom. Therefore, only a univalent metal would form a complete oxide bond to the glass surface by displacing the hydrogen atoms, and the multivalent metals, Mg, Zr and Mo, could not obtain full co-ordination with

oxygen to form the complete oxide bond. Also, the limited oxygen available would not permit a continuous intermediate oxide layer, as observed by Stahl[17], to be formed. Using electron diffraction, Stahl found that, for Al, Be, Mo, Mg and Ni, the intermediate oxide layer was several hundred angstroms thick. Therefore, oxygen must be supplied from another source.

Stahl has suggested that the metallic oxide was formed in the region of the evaporation source, the oxygen being obtained from the residual atmosphere. His investigations were carried out at the relatively high pressure of 10^{-4} mm. Hg. and slow rates of evaporation were used to build up the films step by step. At this pressure, the mean free path of metal atoms in a residual atmosphere of air would be approximately 30 cm., and, with the small source to substrate distance of 1 cm. used by Stahl, there would be very few collisions with the residual gas molecules to give the amount of oxide observed. However, at this pressure 10^{16} molecules of oxygen would strike each cm.^{2} of surface per second[54]. If a film was deposited in this atmosphere to a thickness of 1000A in 60 seconds then approximately 10^{13} atoms of the metal would strike a cm.^{2} of surface per second. Therefore, there would be approximately 1000 oxygen molecules per cm.^{2} per sec. striking the surface

for every metal atom. This would readily allow the formation of oxides and the intermediate oxide layers observed by Stahl would be excessive. The metals examined in the present investigation were deposited at a pressure of approximately 10^{-5} mm. Hg. and at faster rates of evaporation. At this pressure, the mean free path would be approximately 300 cm. and, since the source to substrate distance was 30 cm., again there would be very few collisions with the residual gas molecules. However, these precautions only cut down the ratio of oxygen molecules to metal atoms, striking the surface to approximately 10 to 1. Therefore, the impinging oxygen molecules could still combine with the condensing metal atoms to assist in the formation of the oxide bond to the glass surface or these residual gas molecules could be trapped in the film itself. In this way, by combining with the residual oxygen molecules, metals such as Mg, Zr and Mo could form a complete oxide bond with the glass surface and a continuous intermediate oxide layer could be built up. The heat of formation of these metal oxides per gram atom of oxygen is approximately 100 K.cal/mole, which is about 50 times greater than the van der Waals' forces binding gold and silver films to a glass surface, and this would account for the large difference in adhesion.

Unlike the metals described above, other metals such as Ti, Cr, Ni and Fe showed a marked variation in adhesion with time. The adhesion increased to varying degrees and the time taken appears to indicate that a diffusion process was taking place. It is doubtful whether the increase could be attributed to surface diffusion of the film atoms over the glass surface. These metals do, however, have varying degrees of affinity for oxygen and it would seem that the diffusion process is one which promotes the formation of a continuous intermediate oxide layer between the film and the glass surface. This could be achieved if the oxygen molecules of the residual gas, trapped in the film structure during deposition, could diffuse to the interface to assist in the formation of the oxide layer. Since most films have either an aggregated or a continuous crystalline structure, the diffusion of oxygen molecules would be a feasible supposition. The permeability of the film structure would then be a factor governing the adhesion of a metal film. The increase in adhesion appears, therefore, to be due to the following mechanism. If the metal film was deposited so that there was not a continuous intermediate oxide layer then the adhesion would be poor. However, the adhesion would increase as oxygen molecules diffused through the film structure to

the interface to complete the formation of the intermediate layer. The final adhesion would depend upon the strength of the oxide layer. Further evidence that a diffusion process occurred has been provided by ageing the specimens at an elevated temperature of 120°C. Hill[55] has shown that the increase in adhesion for metal films on glass is more rapid than at room temperature.

The rate of evaporation would also have an effect on the adhesion. A slow rate of film formation would allow maximum combination of the metal atoms with the residual oxygen molecules as well as allowing the trapping of a large number of molecules in the film structure. Therefore, the initial and final values of the adhesion would be higher than those for a rapidly formed film in which the combination with and the trapping of gas molecules would be smaller.

Table 7.3 shows the adhesion of the metals, the rates of evaporation, and the heats of formation of the oxide per gram atom of oxygen[56]. Though, generally, the adhesion for the metals already mentioned appears to be related to the heat of formation of the oxide, there are certain anomalies. However, the adhesion of the metals examined and these apparent anomalies to the proposed theory

TABLE 7.3

The adhesion of metal films to glass and the heat of formation of their oxides

Metal	Adhesion gm. Init.	Final	Rates of Evaporation A/sec.	Heat of Formation of Oxide K.cal./gram atom of oxygen
Mo	5	>500	1.5	65.7
Cr	100	>500	1 - 6	175.6
Ti	5	>500	10	108.7
Zr	200	>500	2	89.4
Fe	100	>500	8 - 10	127.0
Ni	10	200	4 - 22	57.8
Mn	10	400	6 - 40	153.0
Cu	5-30	30	5 - 20	34.9
Au	2	2	1 - 14	-
Ag	6	8	8 - 90	7.0
Al	7	60	2 - 70	266.0
Mg	>500		9 - 13	145.8
Zn	3	8	7 - 14	84.4
Pb	$\frac{3}{4}$	$\frac{3}{4}$	5 - 40	52.5
Cd	5	15	12 - 23	65.2
Sn	2	$\frac{1}{2}$	3 - 12	69.0

can best be explained by dividing the metals into four broad groups as follows:

Group 1.

Group 1 contains the metals Au, Ag and Cu. It has already been mentioned that Au and Ag do not readily form the oxide and that their adhesion to glass, which was poor, was probably due to van der Waals' forces, though, in the case of Ag, the slight increase of adhesion could be due to the formation of a weak oxide bond. On the other hand, Cu forms a fairly strong oxide bond, and, consequently, has a much higher adhesion than either Au or Ag. All these metals have a similar aggregated structure[14] which would allow diffusion of oxygen molecules to the interface. This would account for the rapid increase in adhesion observed with some Cu specimens. The results with Cu also bear out the suggestions made with regard to the rate of deposition. With a fast rate (23 A/sec.), the initial adhesion was poor but was followed by a rapid rise in adhesion. Where the rate was slow, the initial adhesion was high, there being no increase in the adhesion with time.

Group 2.

In Group 2 are the metals Mo, Cr, Ti, Zr, Fe, Ni

and Mg. All these metals form a strong oxide and, with the exception of Ni, cannot be removed from a glass surface after varying periods of time. The high initial adhesions observed in most cases were probably due to the slow rates of evaporation. With the exception of Mg, films of these high melting point metals have a continuous crystalline structure[5] and the increase in adhesion would probably be due to diffusion of oxygen molecules to the interface along grain boundaries rather than through the lattice. The lower value of the heat of formation of the oxide for Ni would account for the slightly lower adhesion observed for films of this metal.

Group 3.

The low melting point metals, Zn, Sn, Cd and Pb, are in this group. The heat of formation of the oxide is reasonably high but the adhesion of these metals to glass was found to be poor. The reason would appear to be due to the film structure. As shown by Levinstein[5], films formed from low melting point metals have highly aggregated structures of large crystals. It has also been shown by Sennett, McLauchlin and Scott[57] that, when cadmium and zinc were evaporated, initial particles as large as 200A appeared on the substrate surface instantaneously, somewhat like a rapid crystallisation. The way in which these particles

grew and the very few nucleating centres formed indicated that the atoms either re-evaporated or migrated over the surface to be linked with atoms already condensed. In the case of Sn, it was shown[58] that surface tension forces affected the structure, the large aggregates being pulled together rather than merging so that an area of surface previously covered was left bare. It is apparent from these investigations that these metals have a cohesion which is much greater than their adhesion to the glass surface. The tendency is to form large separate crystals of regular shape with only a small number of these crystals having any adhesion to the glass surface. The adhesion of these films would therefore be poor.

Group 4.

Group 4 consists of the two metals, Mn and Al. The adhesion results for these two metals were rather surprising since their heats of formation of the oxide are very high and therefore a much higher adhesion to glass would have been expected. The variation of the adhesion with time was similar for the two metals, the adhesion being poor for the first 150 hours but increasing rapidly at this stage to a final value which was lower than anticipated. An explanation of these results to fit in with the ideas so far suggested is rather difficult since

no definite conclusions can be drawn from the results as they stand. However, it will be seen in the following chapters that further evidence was sought by examination of the effect of the residual gas on the adhesion and by observing the structure of these metal films by electron microscopy and their electrical properties.

4. Conclusions

By comparing the adhesion results of films of a large number of metals deposited on a glass surface with the physical and structural properties of the films and the surface, it has been possible to postulate a tentative theory for the mechanism by which most of the metal films adhere to glass. It appears that the adhesion depends upon two main factors, the affinity of the metal for oxygen and the film structure. The metal atoms impinging on the glass surface may either be held to the surface by van der Waals' forces or react with the limited oxygen available in the OH groups on the surface. It is suggested that the role of the residual gas is to supply oxygen so that a complete oxide bond may be formed with the glass surface followed by the formation of a continuous intermediate oxide layer at the interface. However, this layer may not be formed immediately and, in this case, full formation

would probably be dependent upon diffusion of trapped oxygen molecules through the film structure. The rate of formation of the oxide layer and the corresponding increase in adhesion would depend on the permeability of the film structure. Other factors which would affect the adhesion would be the amount of oxygen present in the residual gas, the rate of film formation and the strength of the oxide layer.

Further investigations were carried out to obtain more conclusive evidence for the suggested theory and are described in the following chapters.

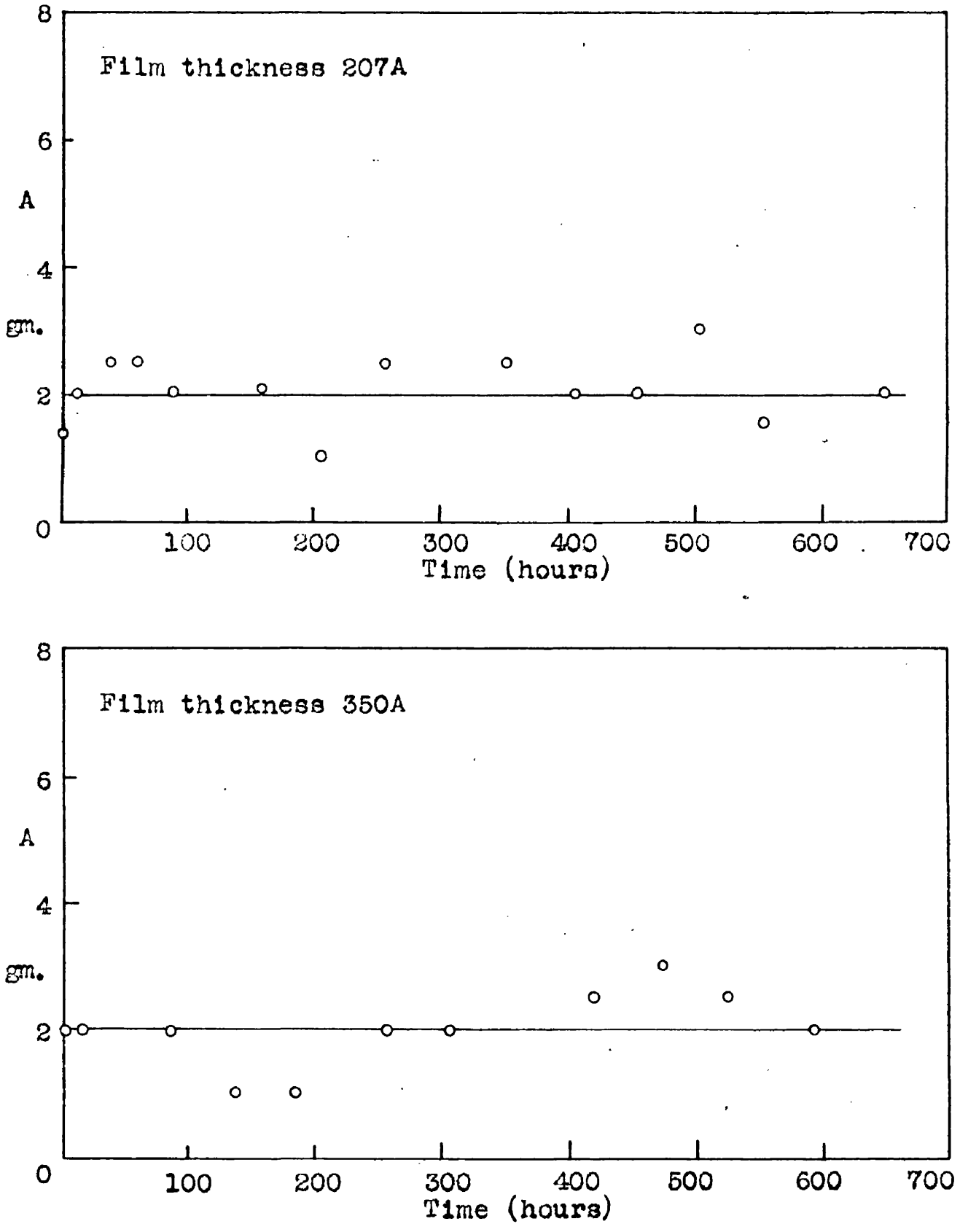
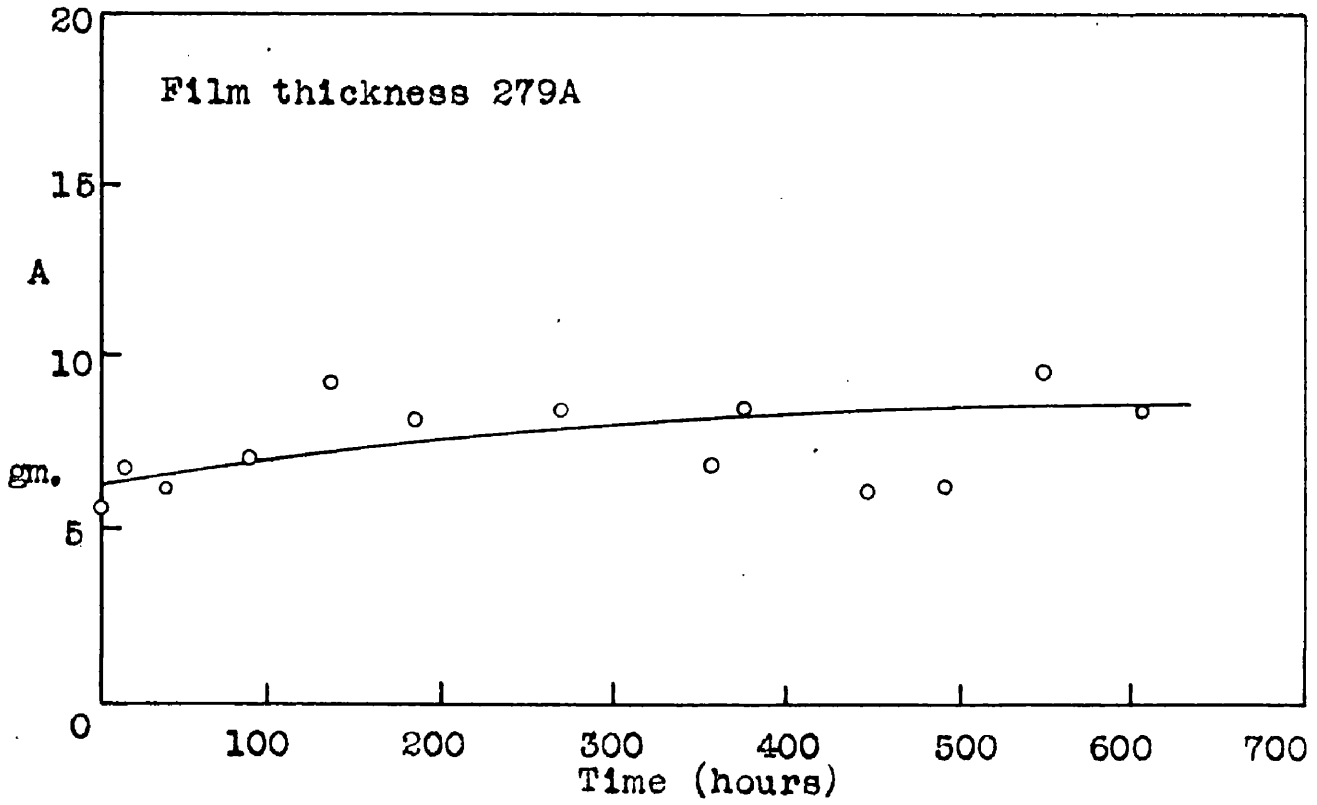


Figure 7.1. Variation of adhesion (A) with time for GOLD films on glass.



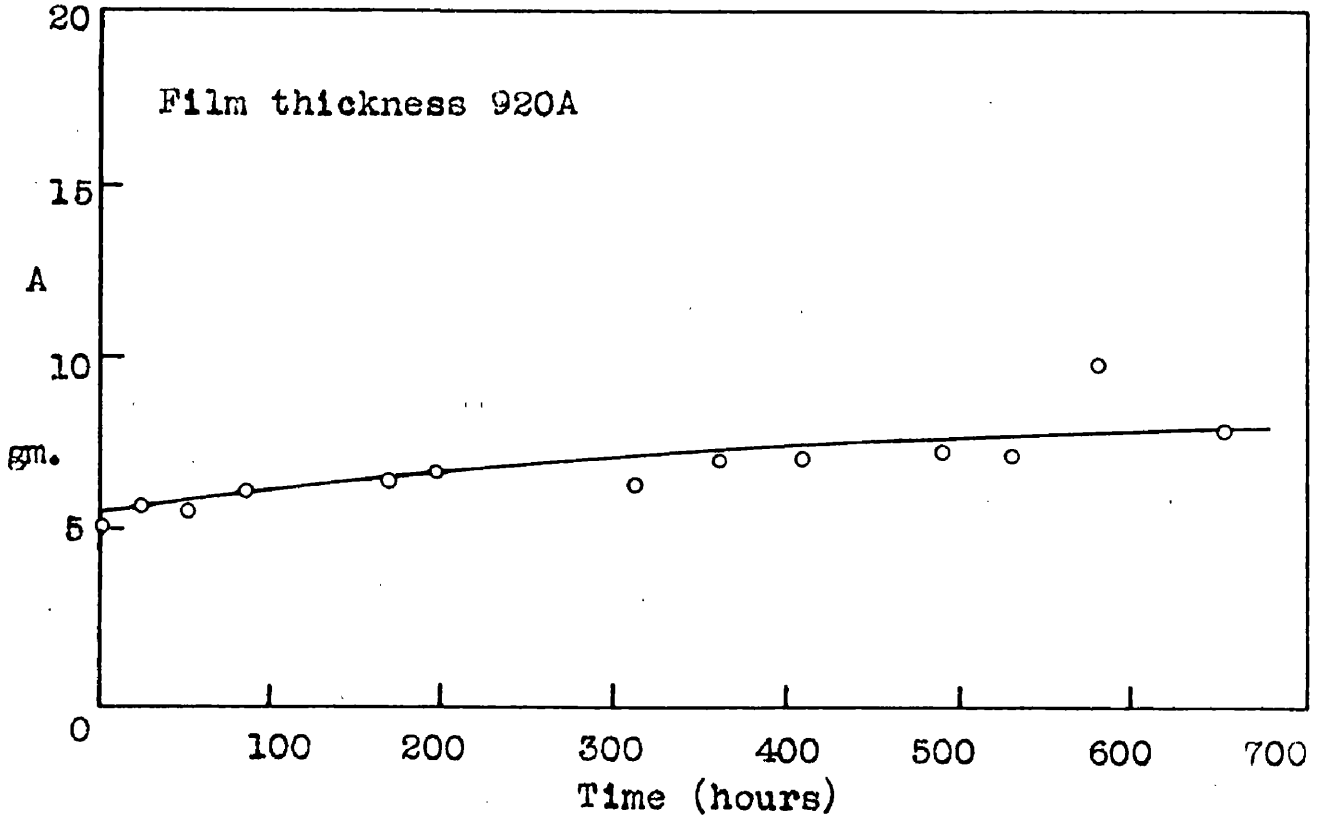


Figure 7.2. Variation of adhesion (A) with time for SILVER films on glass.

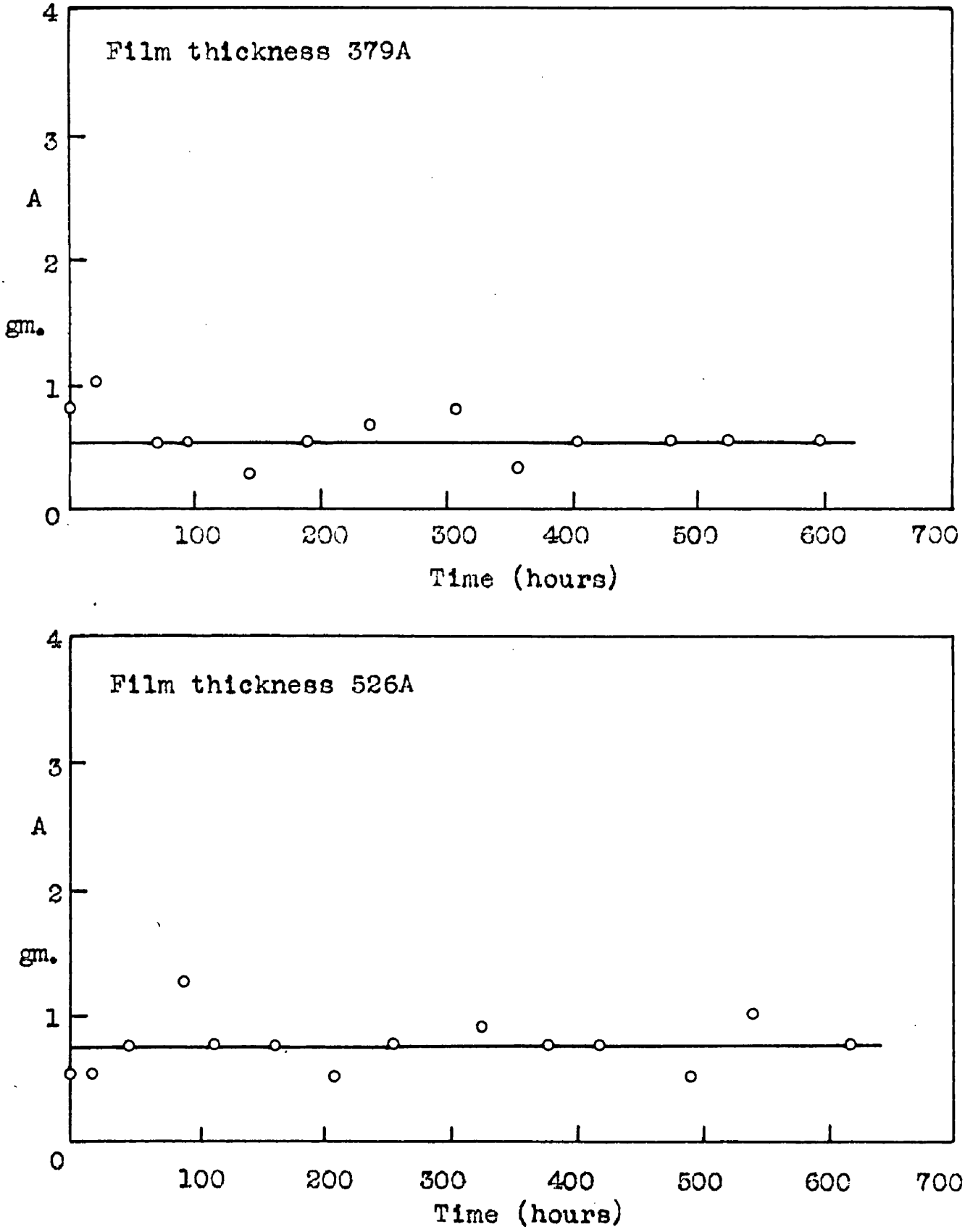
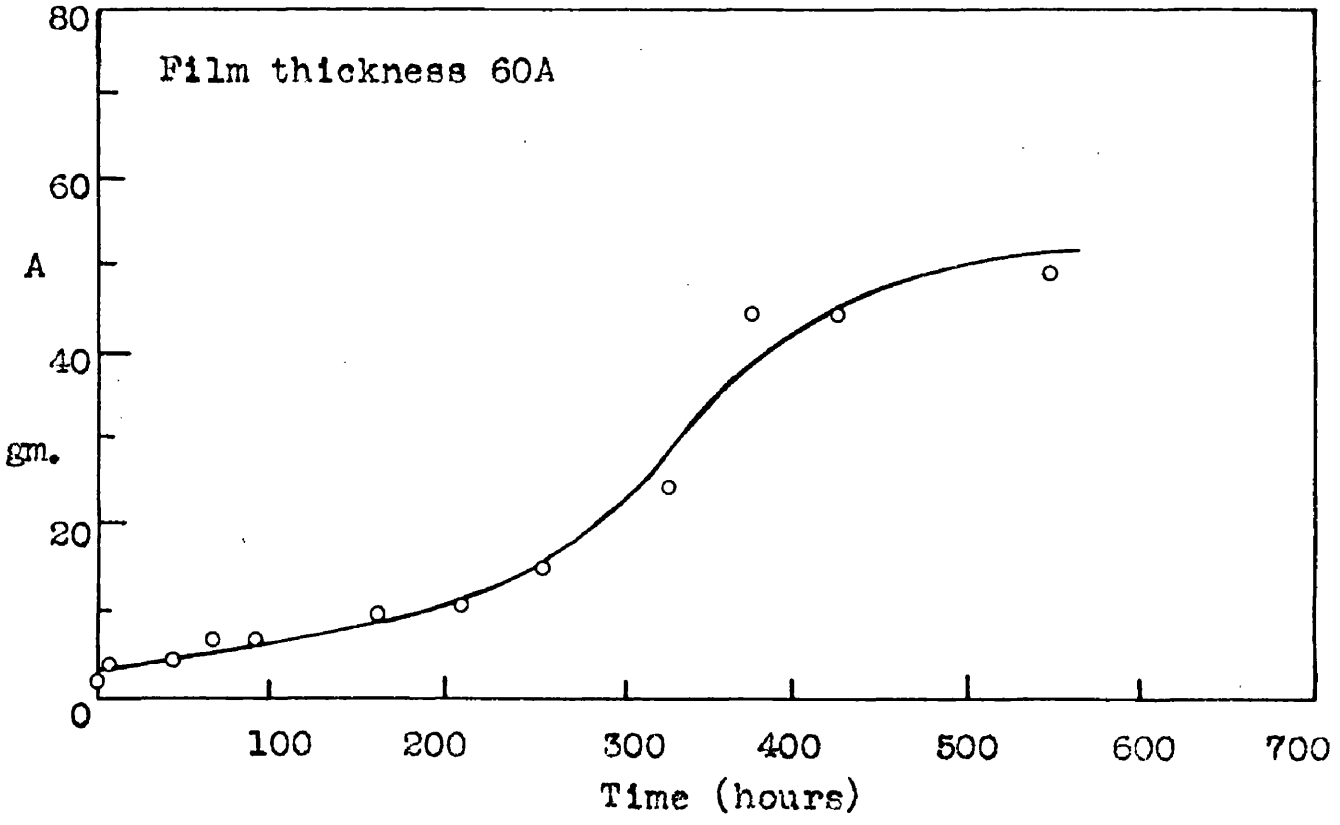


Figure 7.3. Variation of adhesion (A) with time for LEAD films on glass.



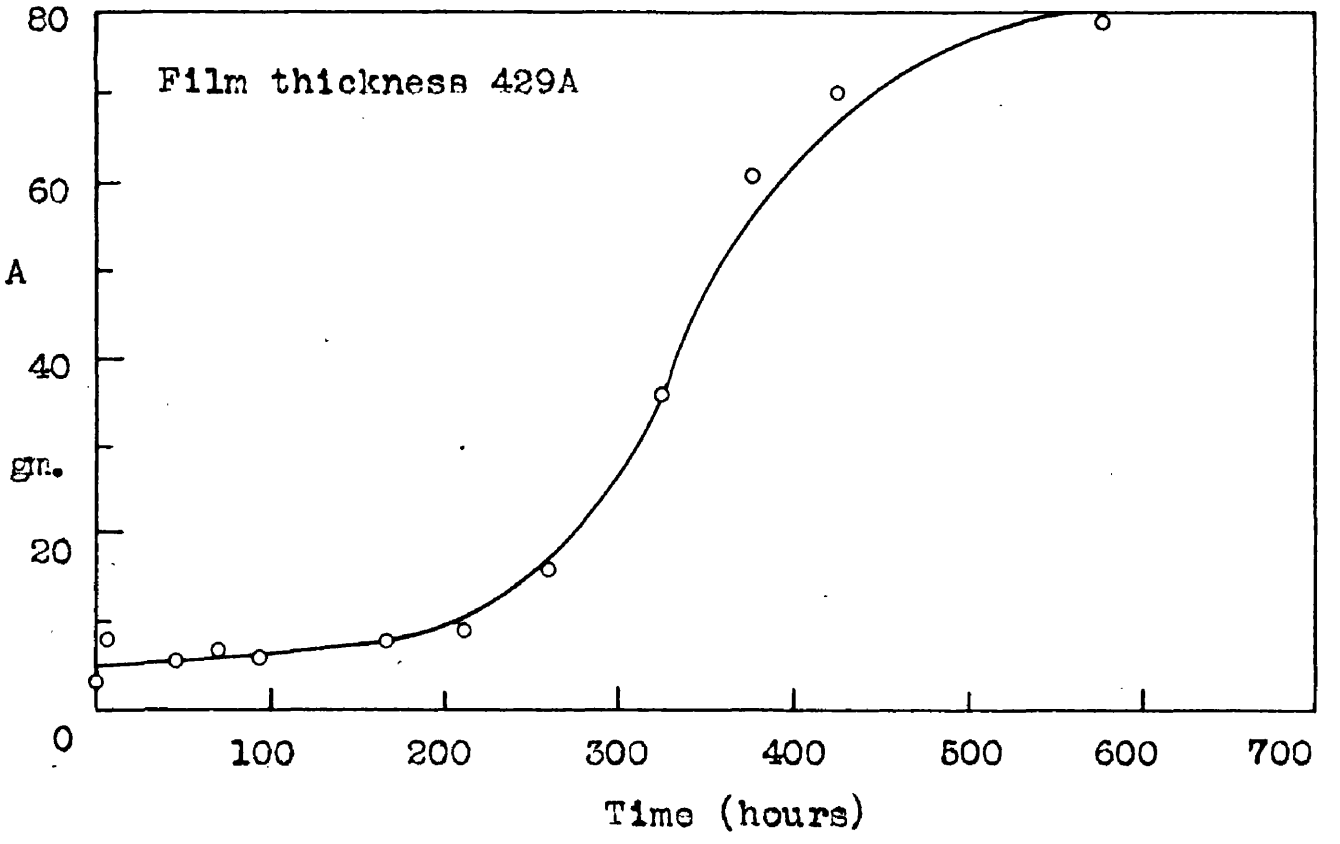
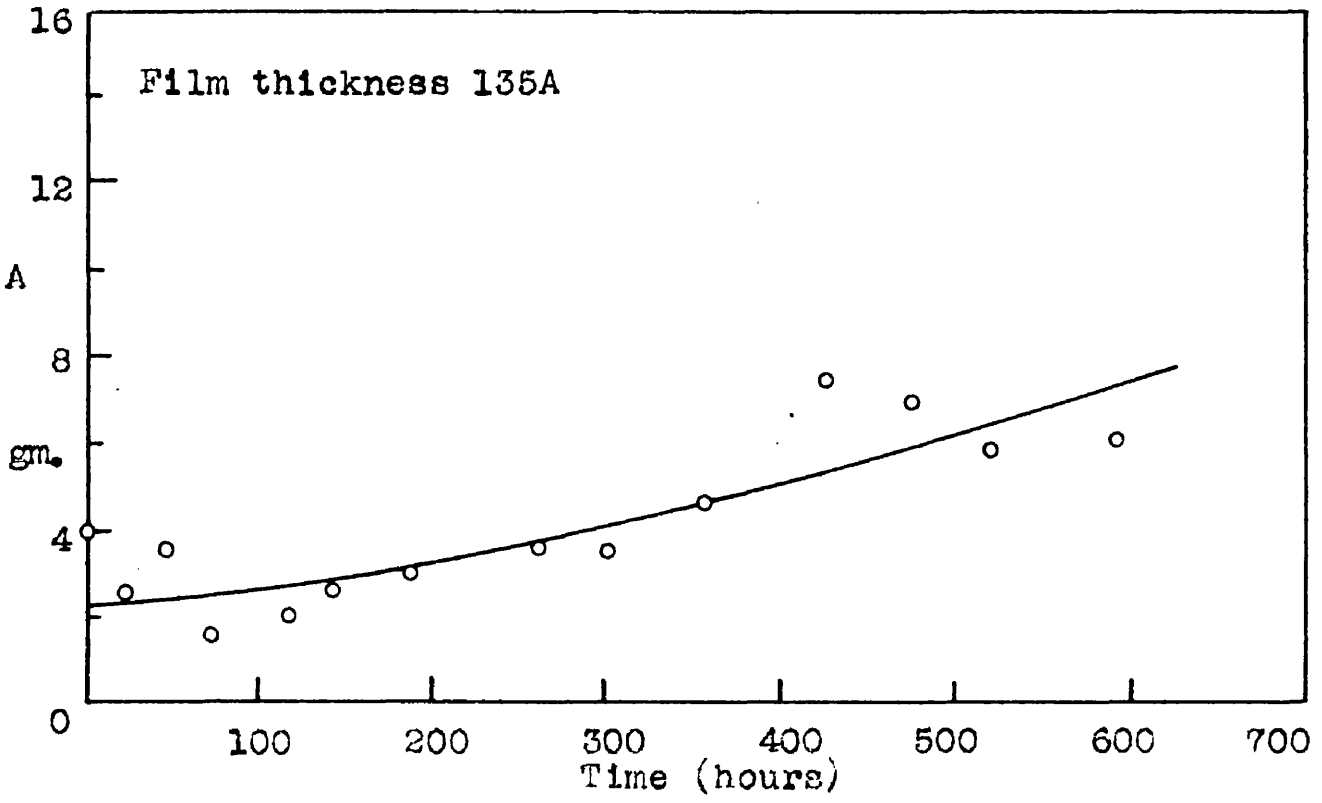


Figure 7.4. Variation of adhesion (A) with time for ALUMINIUM films on glass.



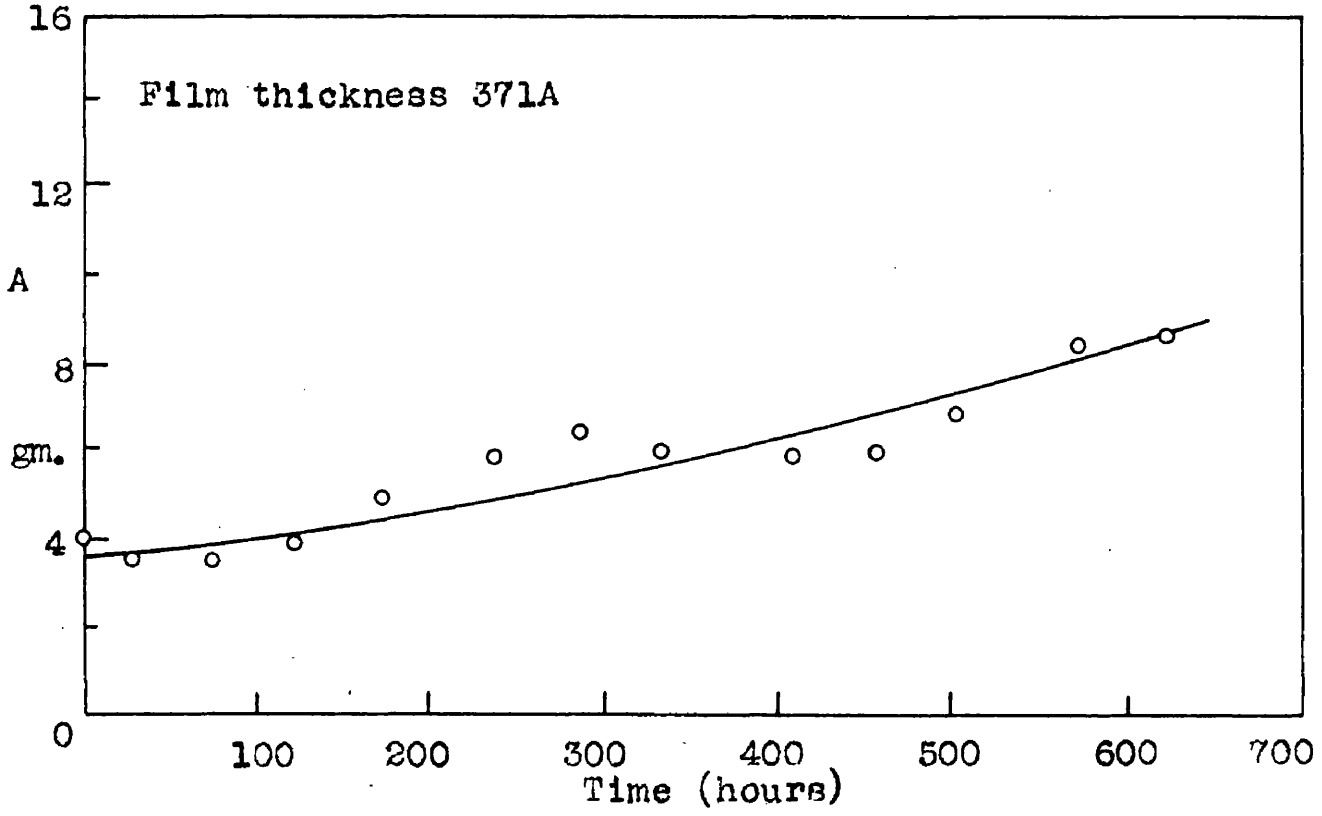
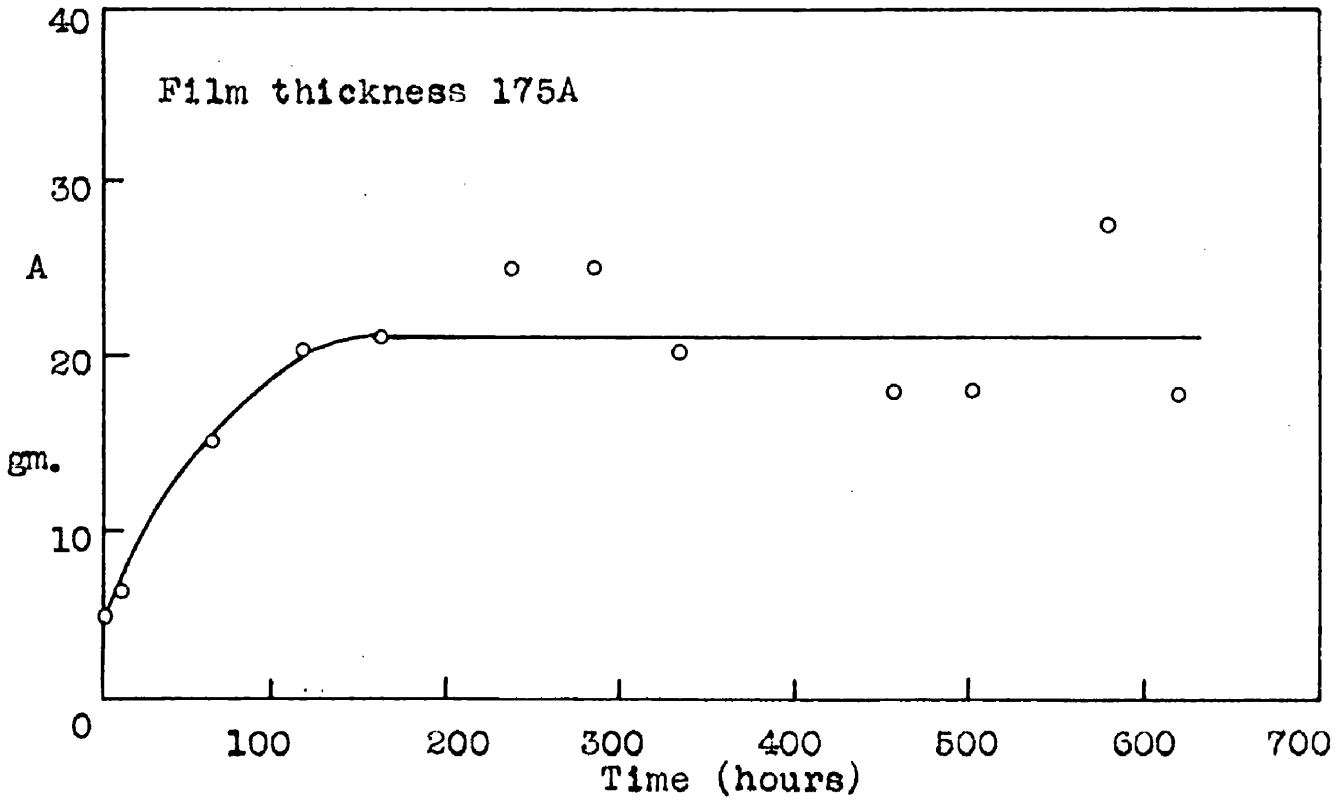


Figure 7.5. Variation of adhesion (A) with time for ZINC films on glass.



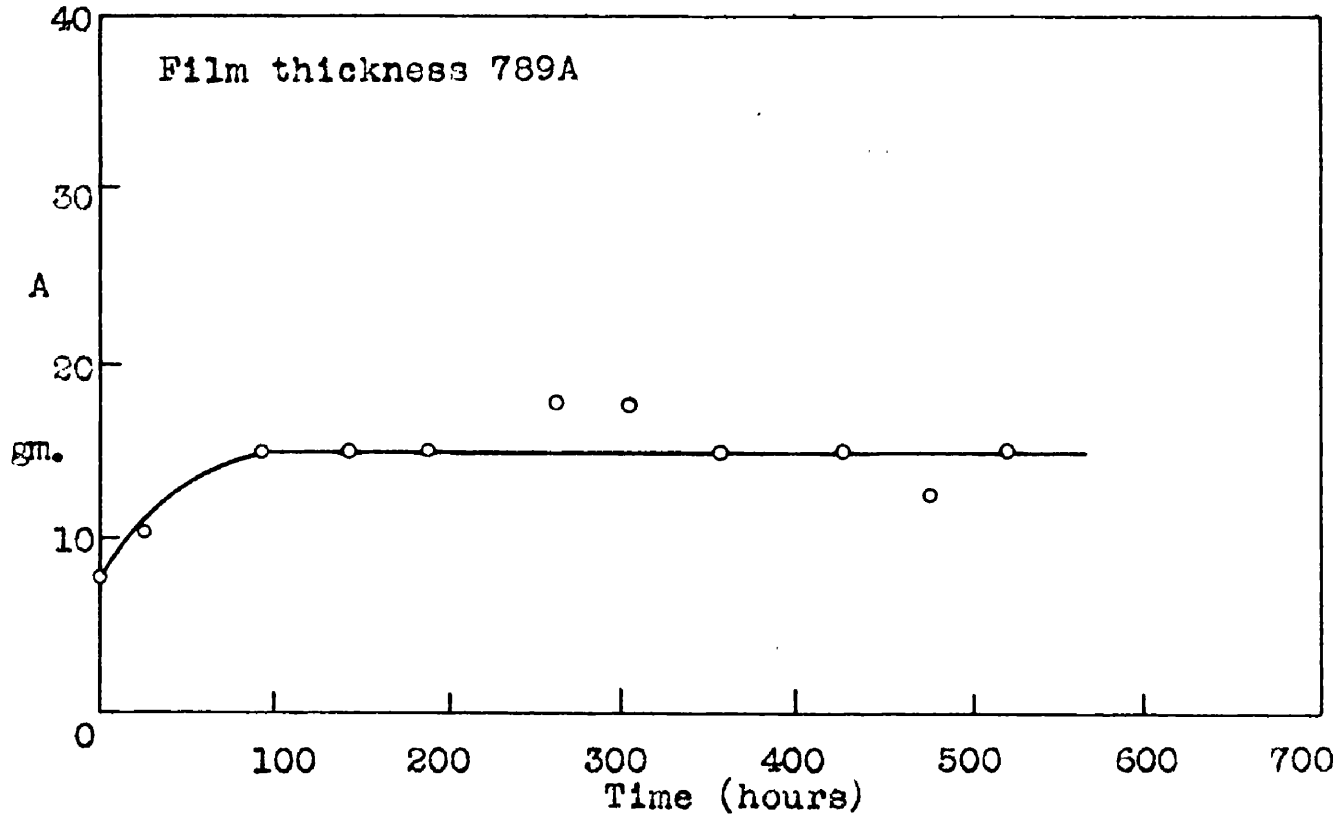
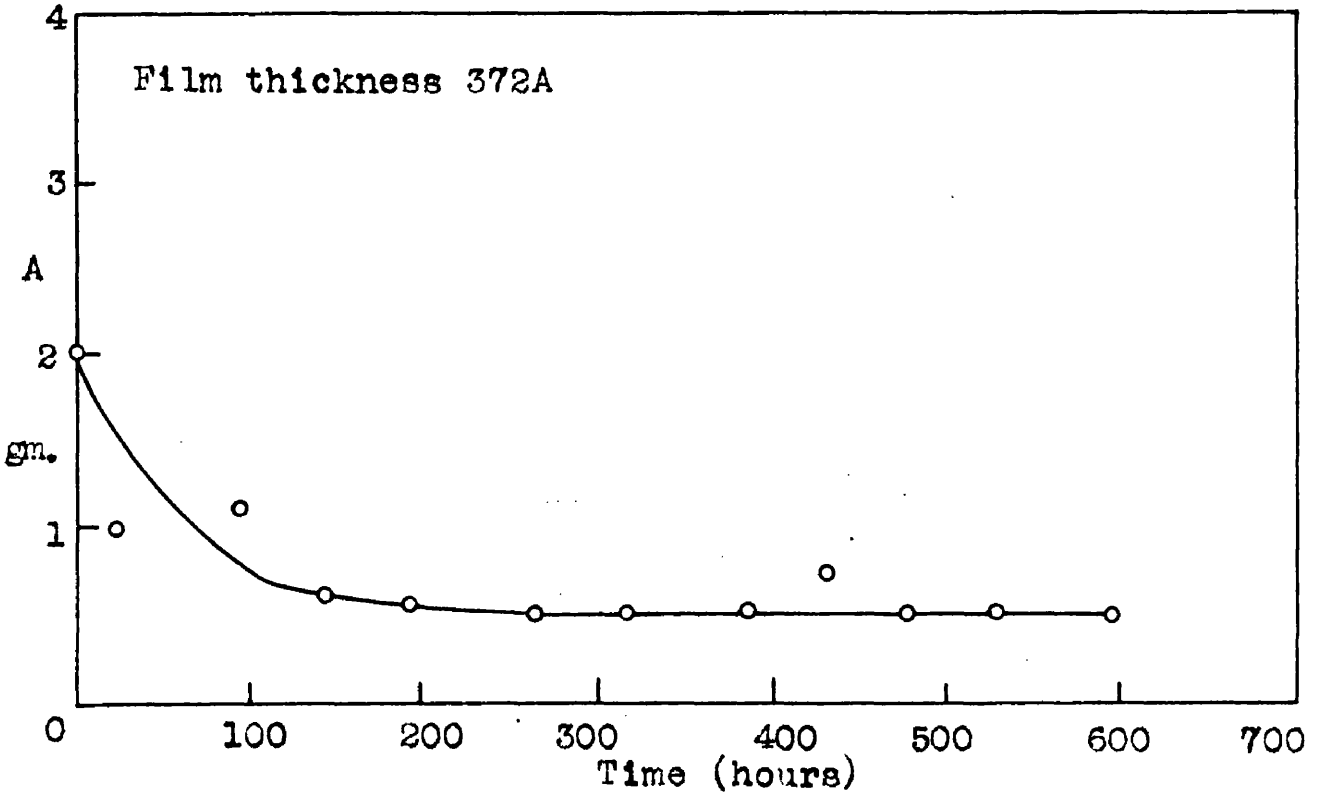


Figure 7.6. Variation of adhesion (A) with time for CADMIUM films on glass.



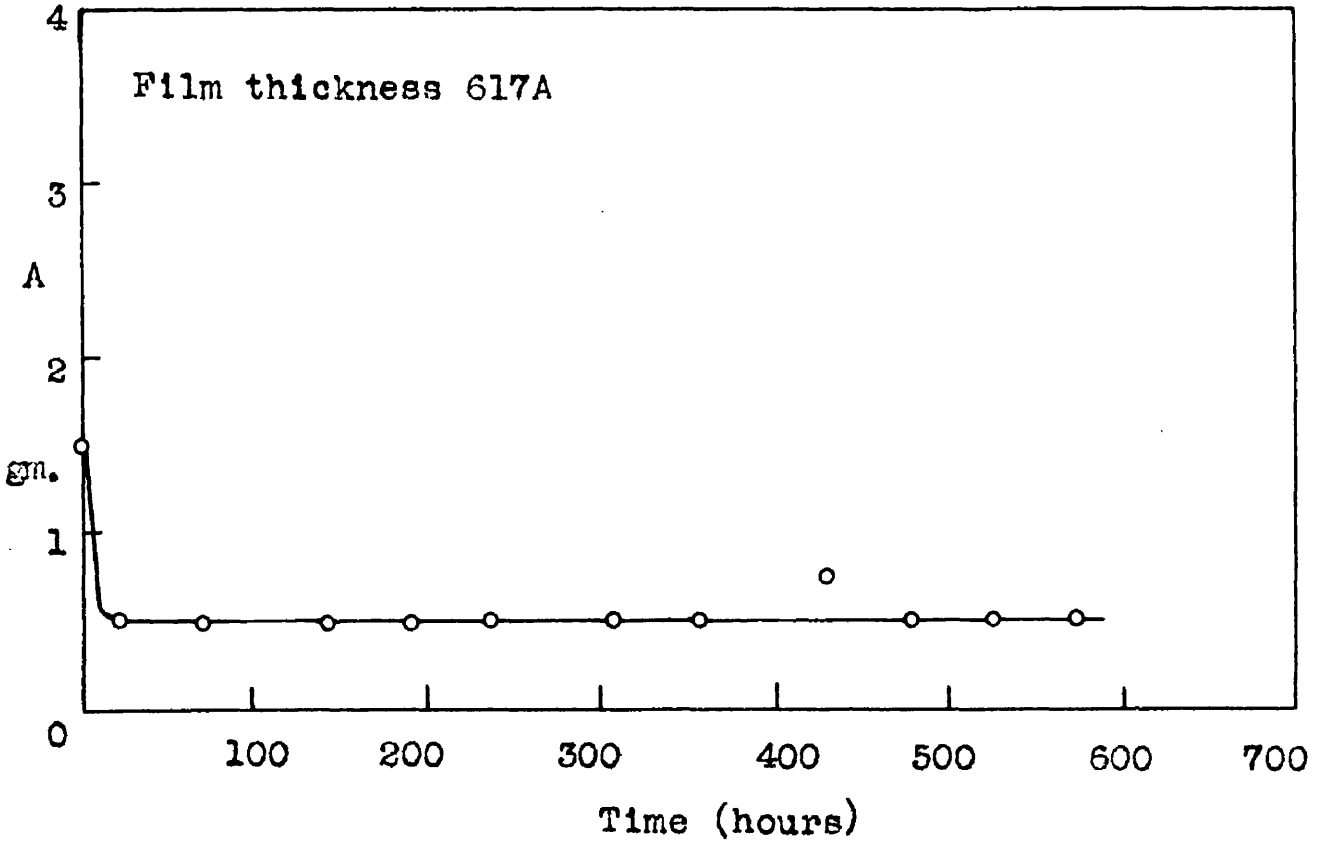
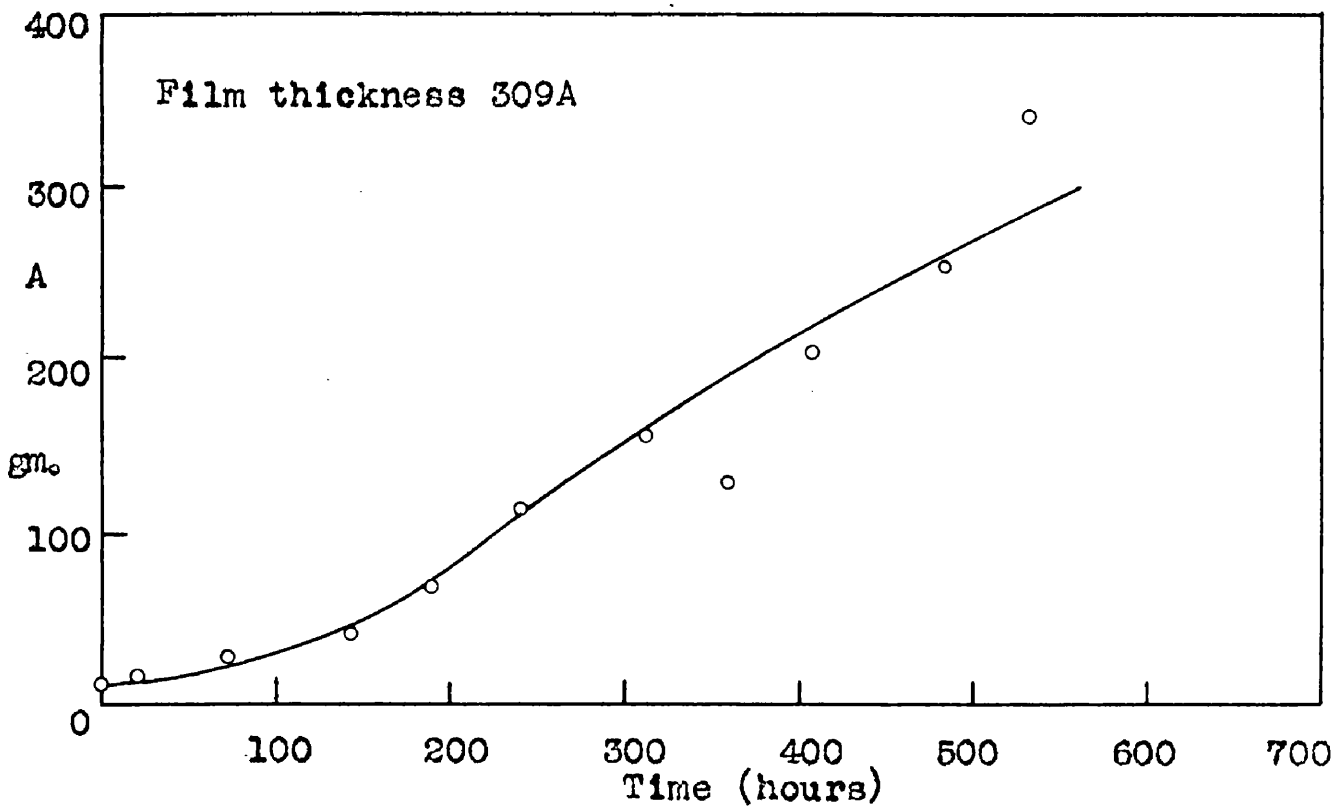


Figure 7.7. Variation of adhesion (A) with time for TIN films on glass.



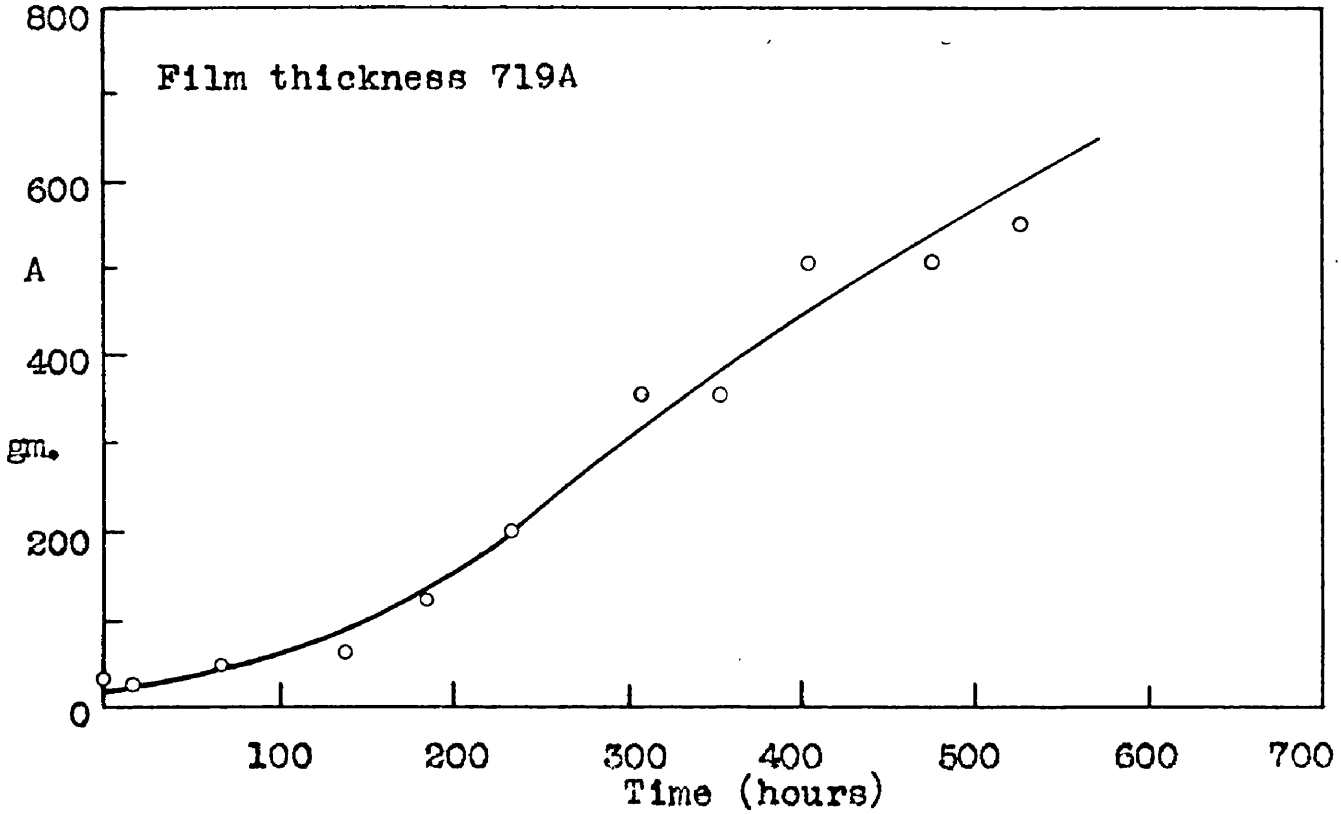


Figure 7.9. Variation of adhesion (A) with time for MANGANESE films on glass.

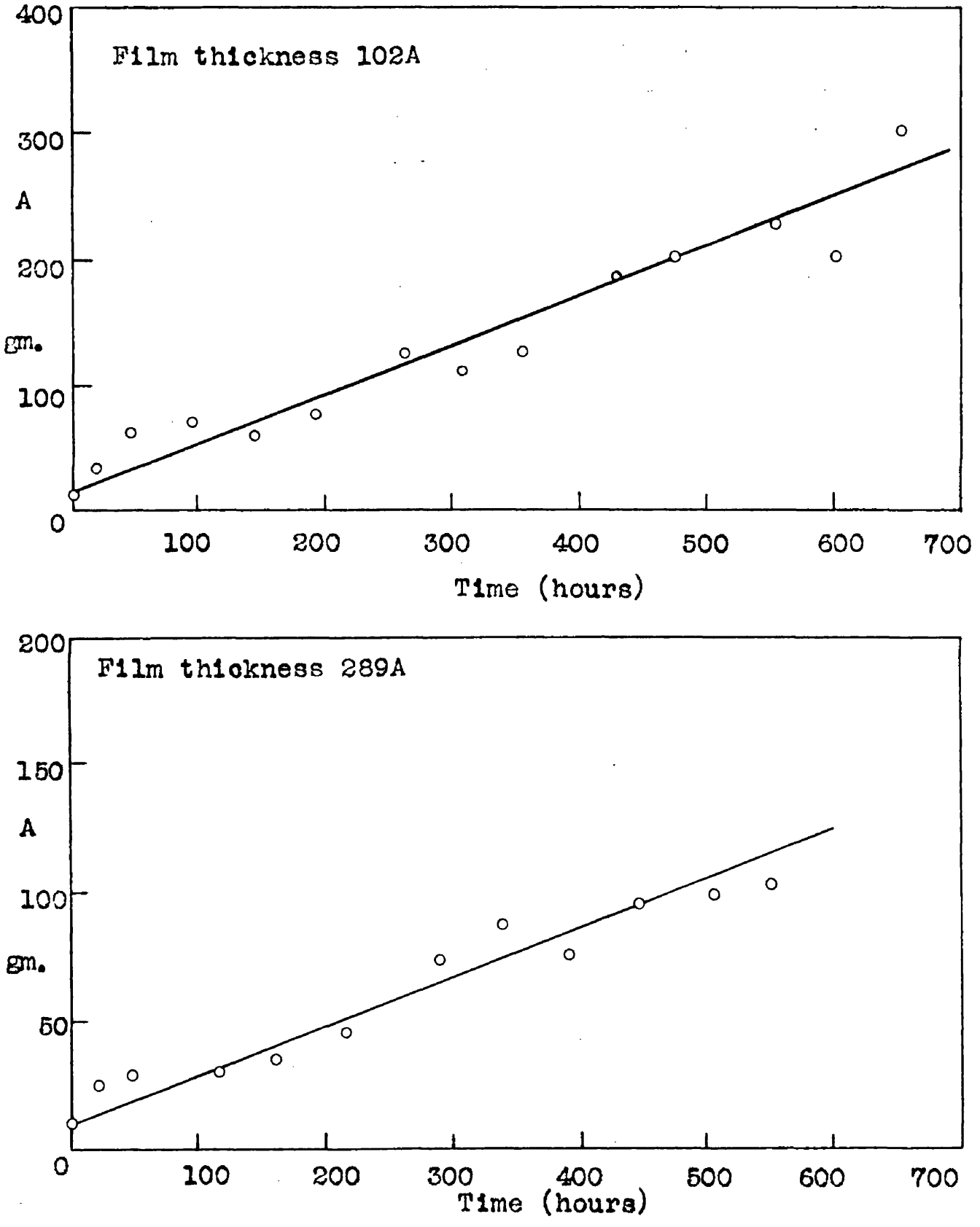
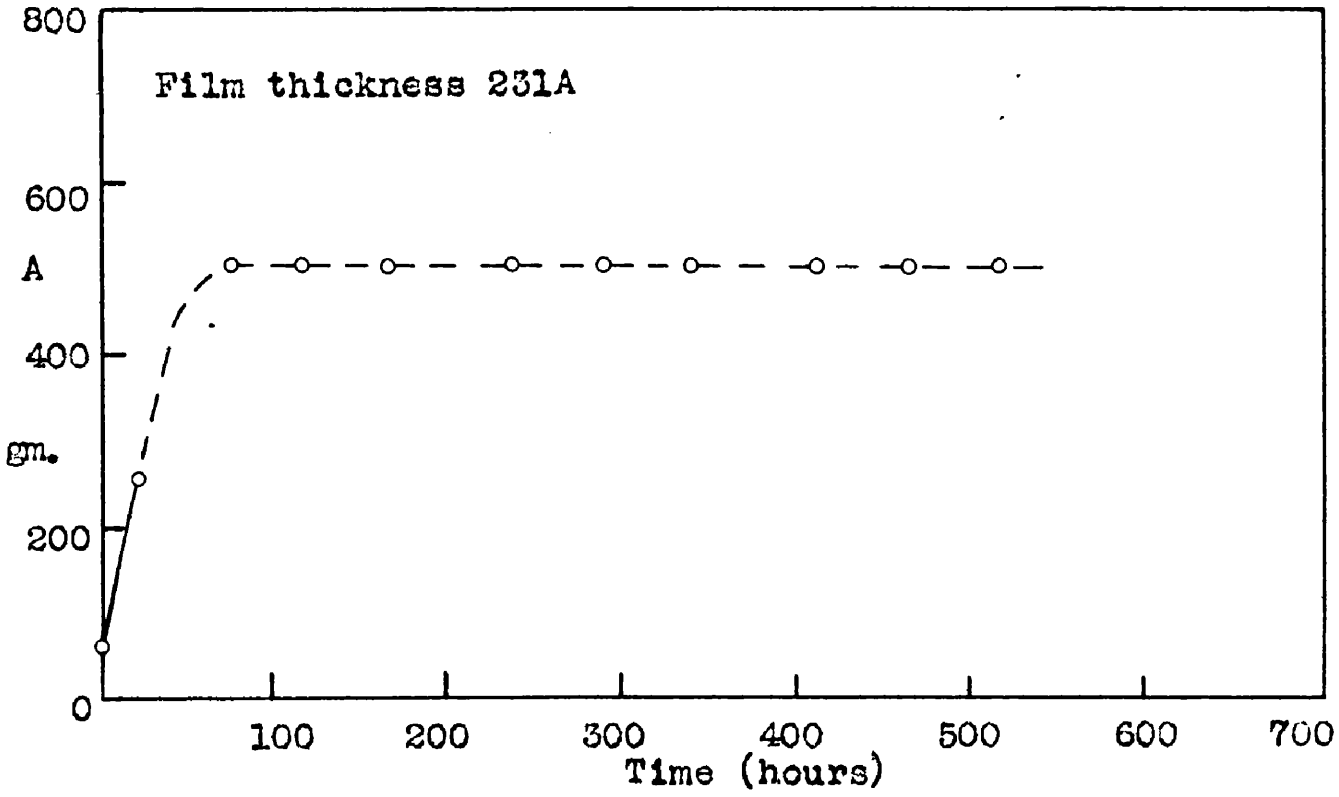


Figure 7.10. Variation of adhesion (A) with time for NICKEL films on glass.



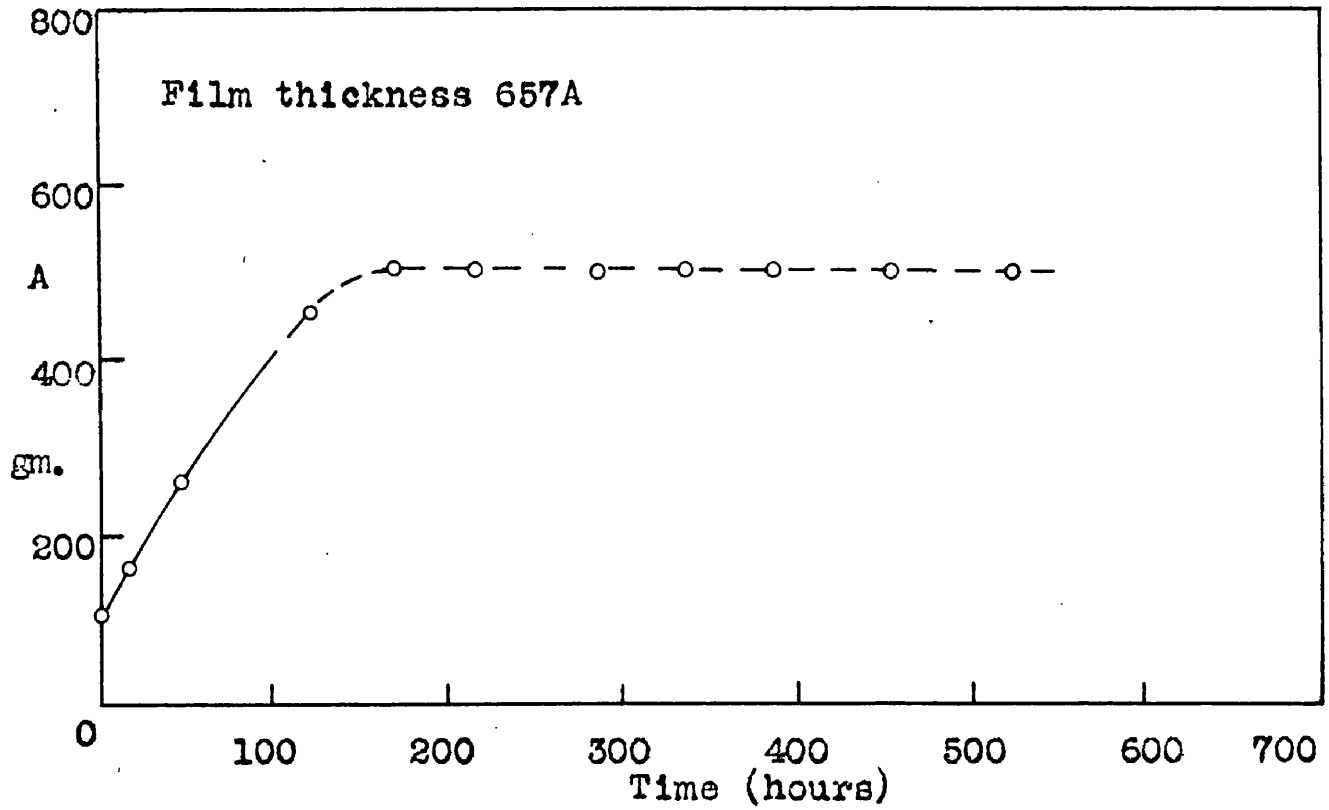
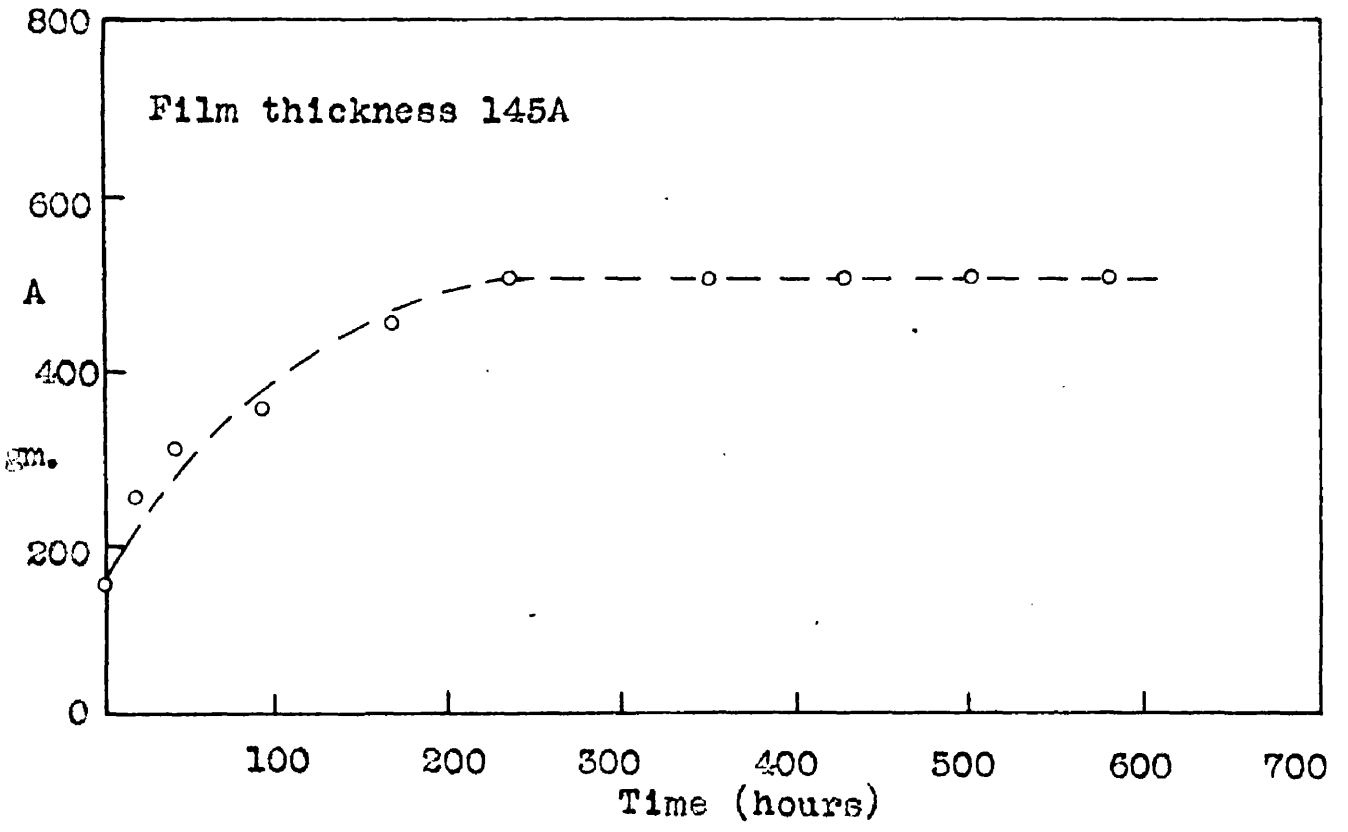


Figure 7.11. Variation of adhesion (A) with time for IRON films on glass.



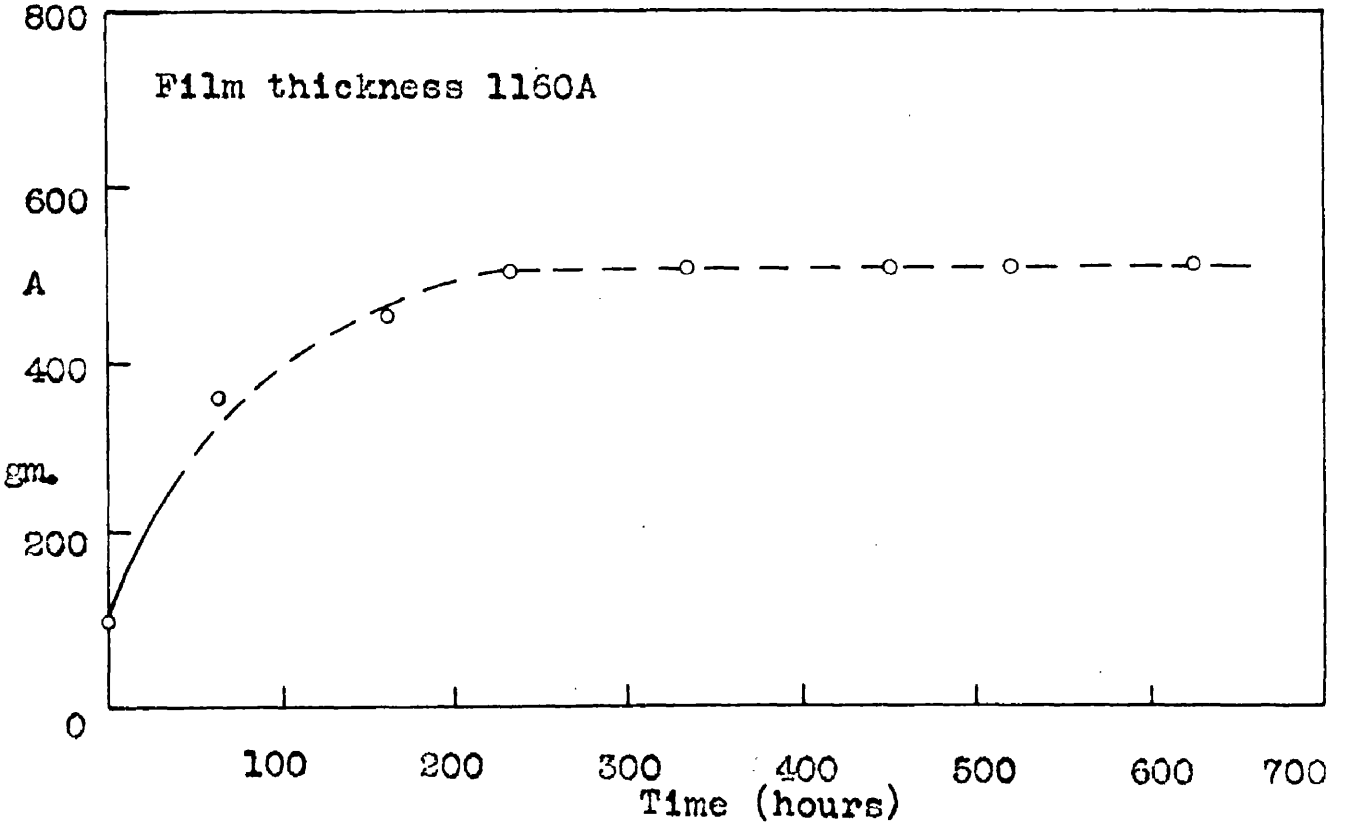


Figure 7.12. Variation of adhesion (A) with time for CHROMIUM films on glass.

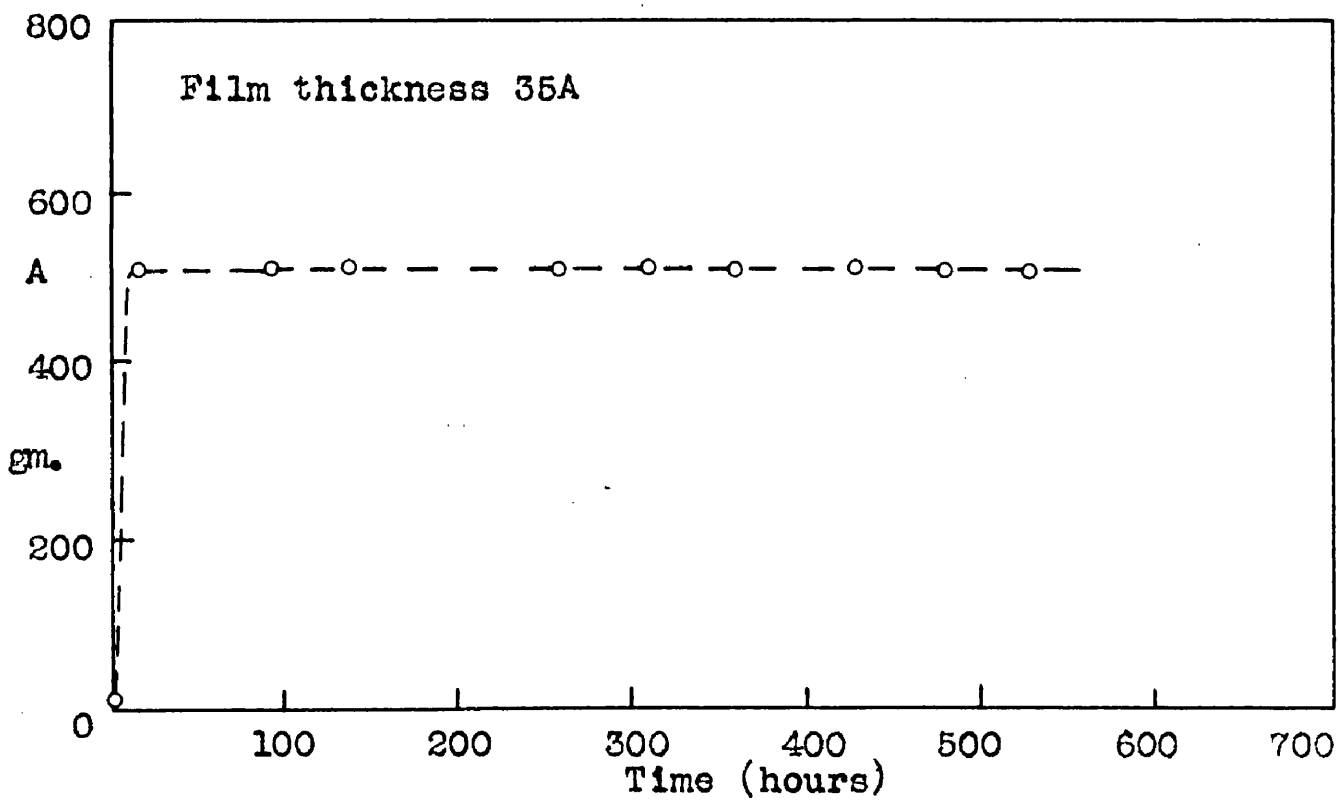


Figure 7.13. Variation of adhesion (A) with time for MOLYBDENUM on glass.

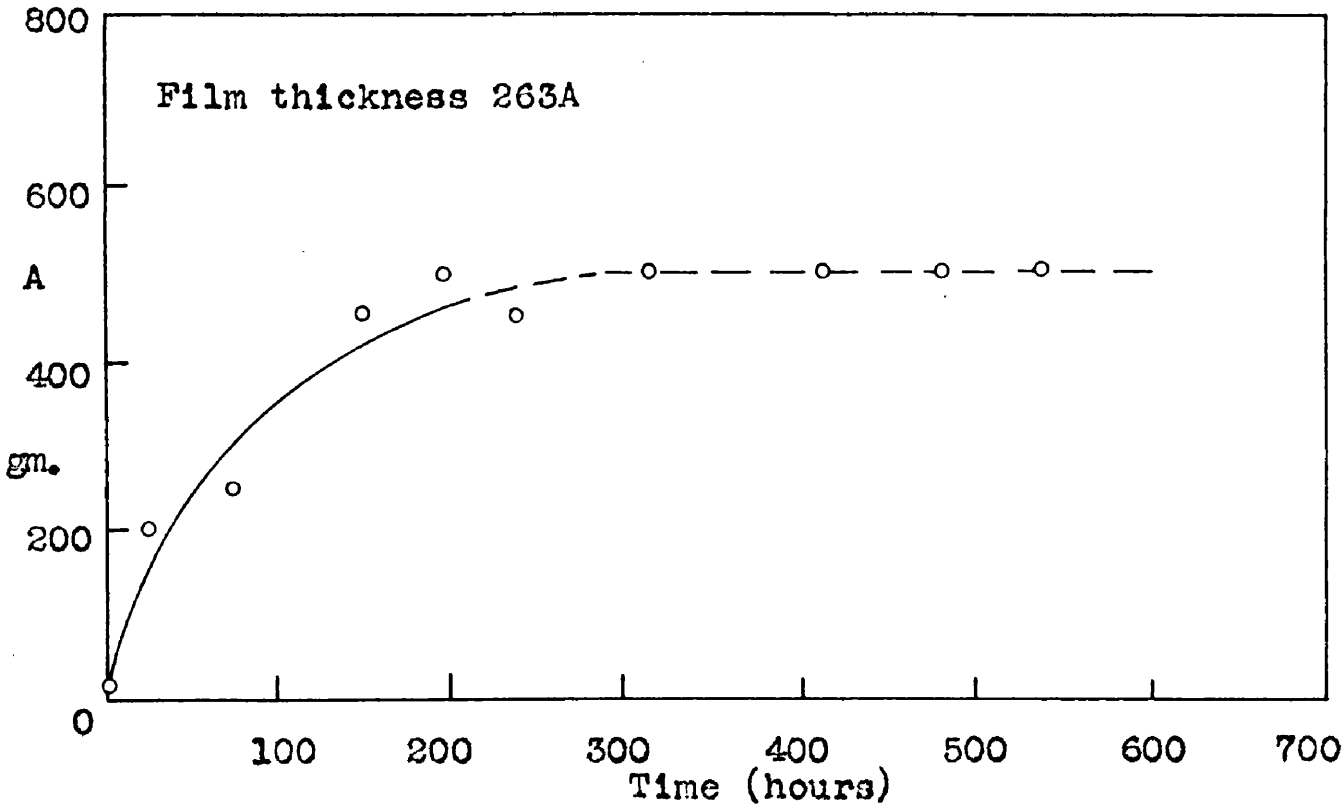


Figure 7.14. Variation of adhesion (A) with time for TITANIUM films on glass.

CHAPTER 8

ADHESION OF METAL FILMS DEPOSITED IN VARIOUS ATMOSPHERES

1. Introduction

In the previous chapter, a theory was proposed to explain the high adhesions and the ageing effects observed with films of a number of metals deposited on glass. It was suggested that oxygen from the residual atmosphere assisted the formation of an oxide bond to the glass surface and that a continuous intermediate oxide layer was built up at the interface. The adhesion of the film would be dependent, among other things, upon the development of this layer and the strength of the oxide bond. The proposed theory implied that the adhesion of a film of an oxygen active metal would be dependent upon the amount of oxygen present in the residual gas.

Therefore, a number of metal films were deposited on glass in atmospheres of air, argon and hydrogen, and their adhesion was measured in the usual manner. These films were prepared either by cathodic sputtering or by evaporation as follows.

2. Experimental

(a) Sputtered Films

Films of Au, Ag, Pt and Cr were sputtered both in air and in argon. When argon was used the chamber was flushed out several times with the gas so that there was a minimum of oxygen present in the residual atmosphere. Depending upon the metal, the films were sputtered at approximately 1 - 2 KV and 5 - 20 mA for 15-60 minutes at pressures of 0.05 - 0.1 mm. Hg. When long sputtering times were used, the deposition was interrupted to prevent overheating the substrate. However, in a number of cases the temperature of the substrate did rise to the order of 75°C.

(b) Evaporated Films

There are certain disadvantages with the sputtering process; for instance, the effect of the continuous glow discharge is not known, the substrate temperature is inclined to rise, and the number of metals which sputter easily is limited. Therefore, the metals Al and Fe were evaporated at high pressures of the order of 10^{-3} mm. Hg. in atmospheres of air and hydrogen. There were two reasons for using this relatively high pressure. Firstly, using air as the residual gas, the concentration of oxygen in the chamber

would be high and the adhesion of oxygen active metals should be affected. Secondly, when hydrogen was used, the high pressure ensured that any oxygen leaking into the chamber was kept to a very small percentage of the residual atmosphere. Also, when hydrogen was used, the chamber was flushed out with this gas before and after outgassing the source material.

3. Results

(a) Sputtered Films

Figures 8.1 and 8.2 show the variation of adhesion with time for films of Pt, Au, Ag and Cr sputtered on to glass in air and in argon. The adhesion of these films definitely appears to have been influenced by the nature of the residual gas. It can be seen that, in all cases, the adhesion for films sputtered in air was higher than the adhesion for films sputtered in argon. Only films of Au and Ag showed any ageing effects and even then the change was only small. The nature of the residual gas had the biggest effect on chromium. Cr films, sputtered in air, could not be removed from the glass surface, whereas, when this metal was sputtered in argon, the films had a very poor adhesion.

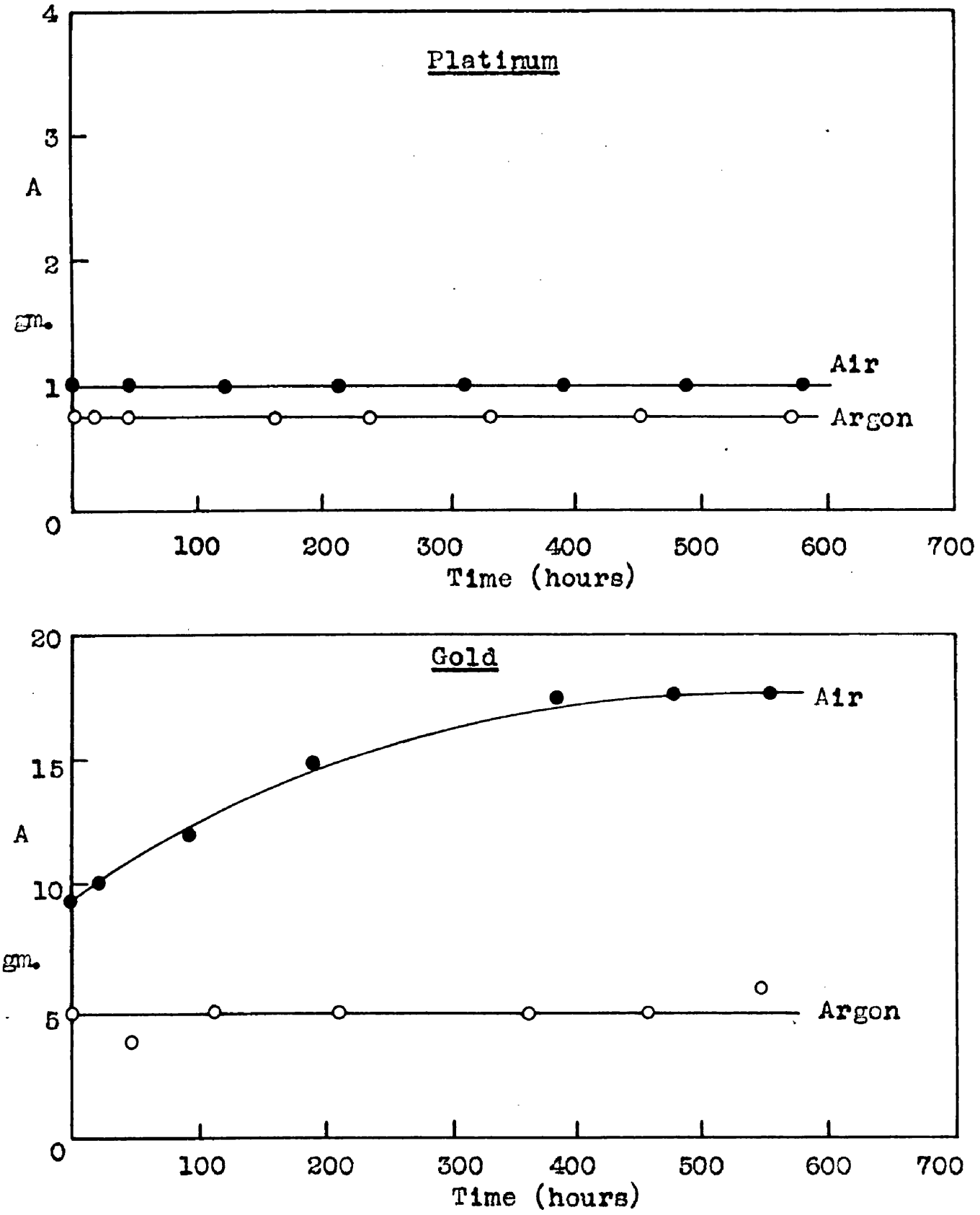


Figure 8.1. Variation of adhesion (A) with time for metal films sputtered on glass in various atmospheres.

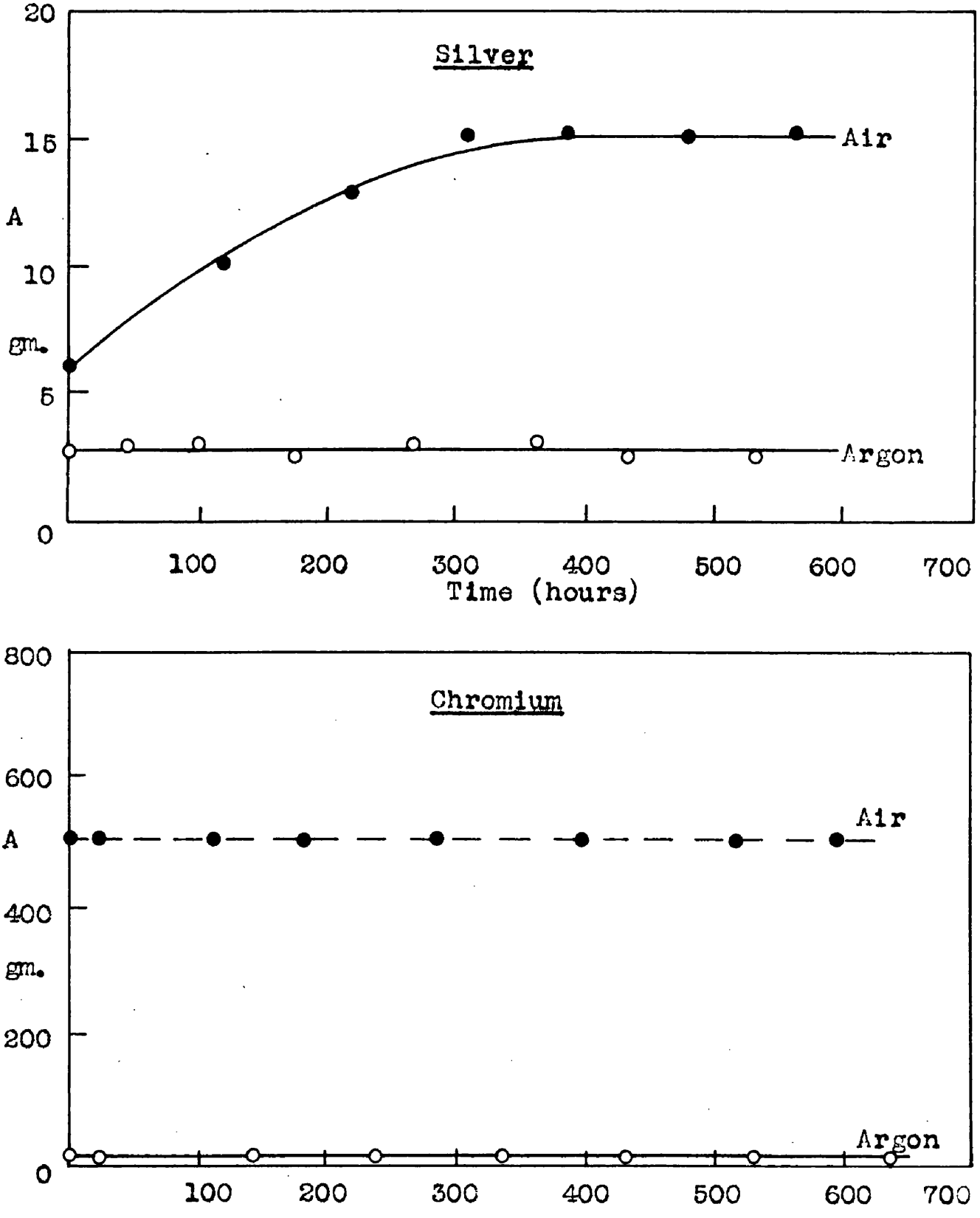


Figure 8.2. Variation of adhesion (A) with time for metal films sputtered on glass in various atmospheres.

(b) Evaporated Films

The results for Al and Fe films deposited by evaporation in atmospheres of air and hydrogen are shown in Figures 8.3 and 8.4. Once again the effect of the residual gas can clearly be seen. When deposited in an excessive atmosphere of oxygen, Al was found to be non-removable. However, when Al was deposited in an oxygen free atmosphere, the films were readily removed and showed little or no increase in adhesion with time. The results for Fe were similar. Films deposited in air had a very high initial adhesion and soon became non-removable, whereas, those deposited in hydrogen had a much lower initial adhesion which did not increase greatly with time.

By superimposing on Figures 8.3 and 8.4 typical adhesion results for films of these metals deposited at 10^{-5} mm. Hg., the effect of increasing the amount of oxygen present during deposition on the adhesion of these films can be seen. The amount of oxygen would be negligible in an atmosphere of hydrogen at 10^{-3} mm. Hg., whereas, in an atmosphere of air at pressures of 10^{-5} and 10^{-3} mm. Hg., the ratios of the number of oxygen molecules to the number of metal atoms striking a cm.^{2} of surface per second would be approximately 10:1 and 10^3:1 respectively. The

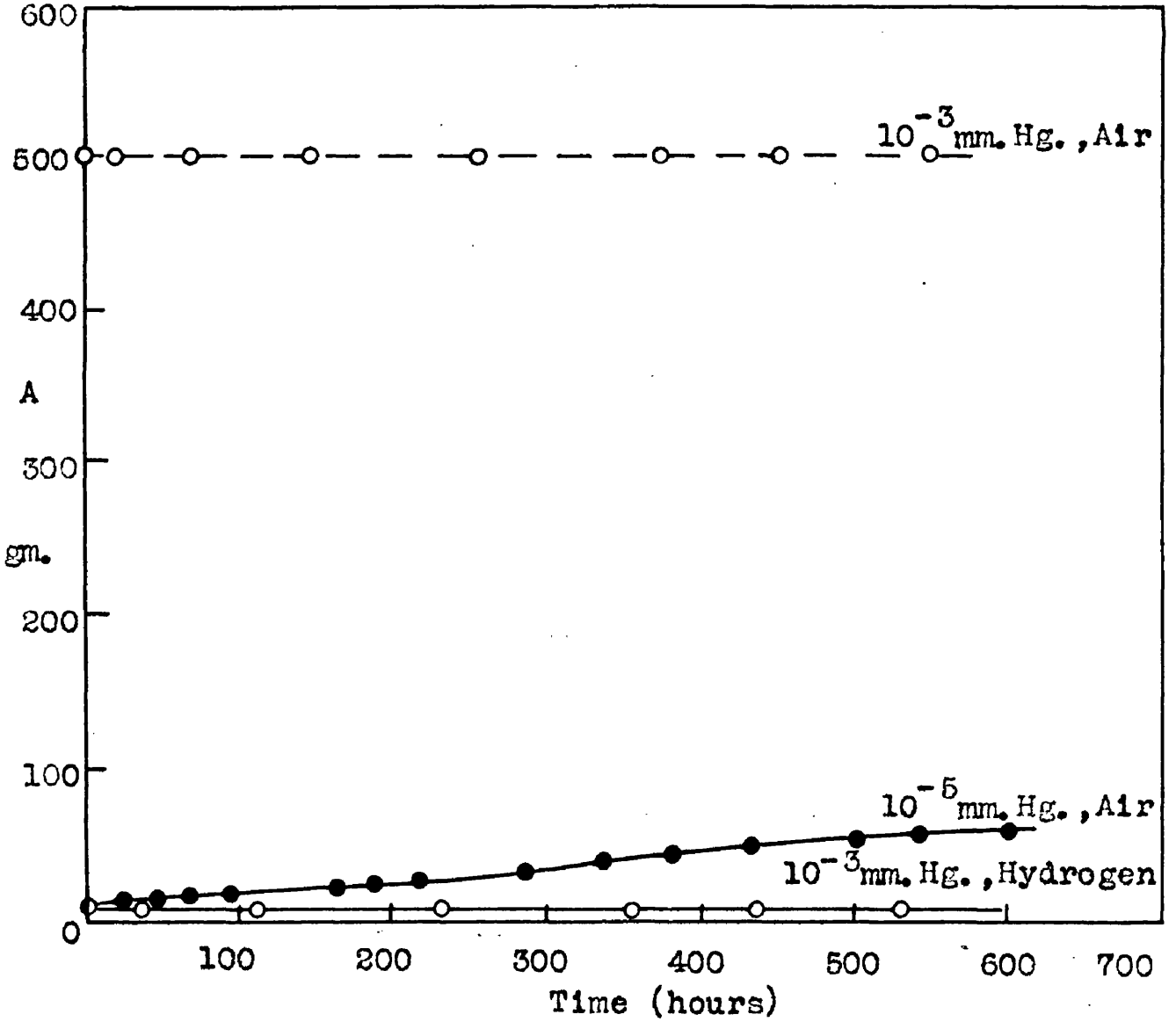


Figure 8.3. Variation of adhesion (A) with time ALUMINIUM films deposited on glass in various atmospheres and at various pressures.

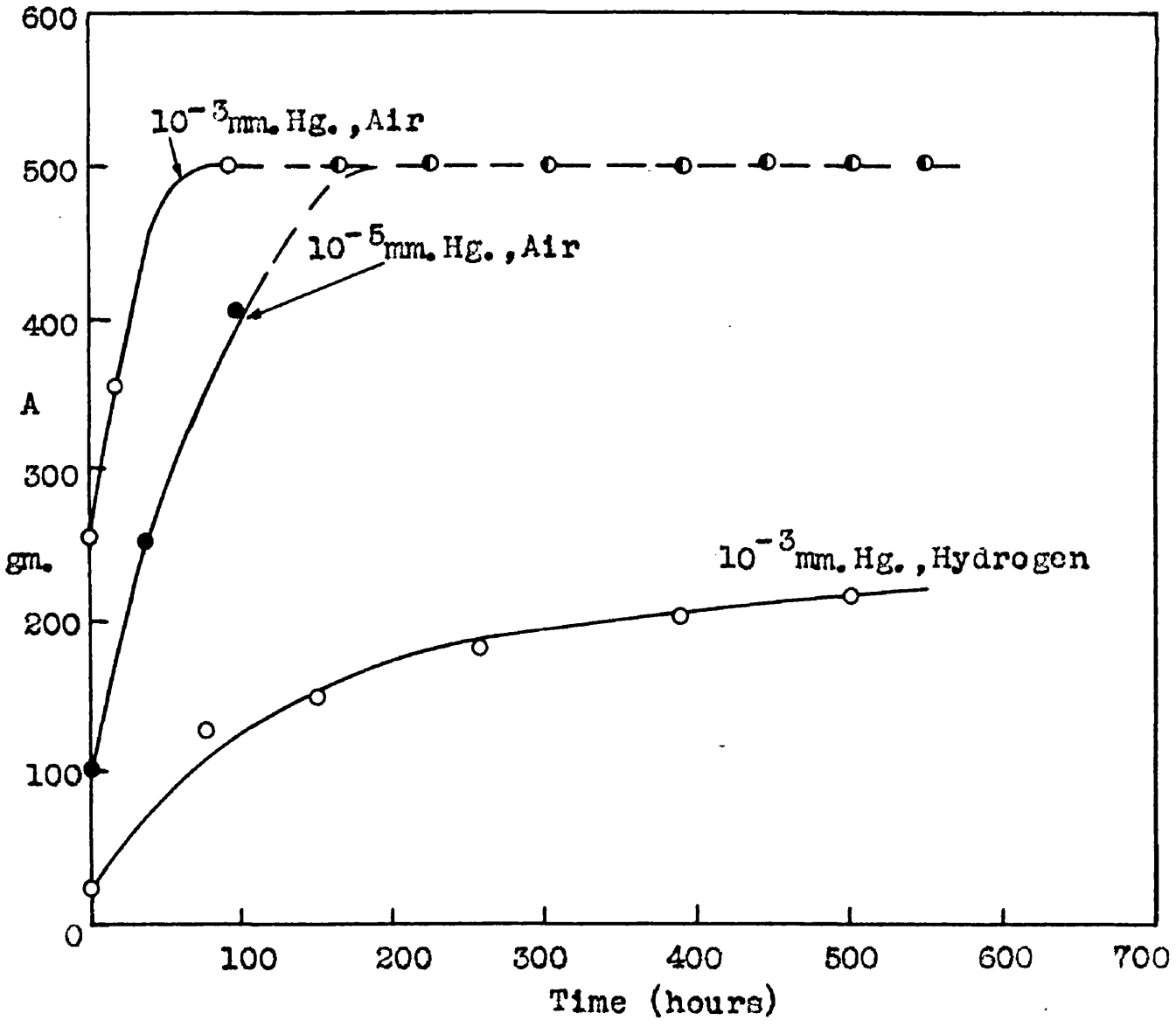


Figure 8.4. Variation of adhesion (A) with time for IRON films on glass deposited in various atmospheres and at various pressures.

corresponding increases in the adhesion of films deposited in these atmospheres can clearly be seen.

4. Conclusions

This investigation has shown that the adhesion of metal films to glass was dependent upon the nature and pressure of the residual gas in which they were deposited. The effect on the adhesion of the amount of oxygen present in the chamber during deposition was clearly shown by the results of the adhesion measurements on Al and Fe. It would appear that the tentative theory, proposing that the adhesion of a metal film to glass would be enhanced by the formation of an intermediate oxide layer at the glass surface and that the formation of this layer would be assisted by oxygen from the residual atmosphere, has been verified.

CHAPTER 9

STRUCTURE OF THIN METALLIC FILMS

1. Introduction

It has been shown that the adhesion of a metal film to glass appears to be dependent upon the affinity of the metal for oxygen and the formation of an intermediate oxide layer at the metal-glass interface. It is possible, however, that the structure of the film would also be a factor governing the adhesion, explaining the increase in adhesion with time observed with films of a number of metals and the poor adhesion observed with the low melting point metals. Though a vast amount of work has been carried out on the structure of thin metallic films, it was felt that, since the film structure played such an important role in explaining the adhesion, the structure of the films prepared under the conditions used in the present investigation should be examined.

The best method for this examination is the direct observation of the film structure in an electron microscope in conjunction with electron diffraction. While the microscope shows the actual shape of the particles making up

the film, electron diffraction enables structure of these particles to be examined. For example, if the pattern consists of very diffuse rings then the film may be in either an amorphous or a microcrystalline state. On the other hand, if the pattern consists of very sharp rings then the film has large crystalline areas. The continuity of the rings indicates to some extent the orientation of the crystallites, while the diameter and width of the rings give an estimate of the structure and size of the crystallites.

Specimen films of a number of metals were prepared under the usual conditions employed in the present investigation and their structures examined in an electron microscope. Since every detail in the structure of these films, such as grain boundaries and aggregation, had to be examined the resolution of the microscope was important. Therefore, these films were examined in a Siemens Elmiskop microscope which gave a resolution of approximately 12A. The use of this microscope was by the kind permission of the Physical Chemistry Department of the University of Glasgow, and therefore only a limited number of specimens could be examined. The diffraction patterns of the specimens were observed in a Metropolitan-Vickers E.M.3. electron microscope in this department since a high

resolution was not required for this type of investigation.

2. Preparation of Specimens

The film structure was examined in the microscope by transmission and therefore the films to be examined could not be deposited on to a glass substrate but had to be deposited on to an organic material which was relatively transparent to the electron beam. Sennett and Scott[41] have shown that formvar is the best organic material for this type of investigation since the structure of metal films was found to be the same on this material as on glass. Consequently, formvar was used in this investigation as the substrate.

These formvar substrates had to be thin and of uniform thickness so that maximum illumination and even contrast was obtained on the viewing screen. Therefore, the formvar films were prepared in the following manner.

A solution was made up of 0.4% formvar in dioxan. A small quantity of this solution was spread evenly on a clean microscope slide and allowed to dry. The formvar film was then cut into sections and these sections were floated off on to the surface of distilled water. A copper grid of fine mesh (200 mesh/inch) was placed on a fine gauze and brought up under a selected formvar section so that, as

the gauze was removed from the water, the formvar film covered the grid. The excess water was removed and the formvar was cut away round the grid which was removed and placed in a copper cap. This method gave formvar films of a uniform thickness of approximately 100-150A. These films were dried and stored in a dessicator until required though they were never kept unused for longer than a few days.

When required, the grid was positioned next to a glass blank in the evaporation chamber at the usual height above the source. The chamber was cleaned out with a glow discharge to which the formvar film was also exposed. A metal film was then deposited on the formvar and the glass blank under the usual conditions. The grid was removed and stored in a dessicator until it could be examined in the electron microscope while the metal film on the glass blank was used for determining the film thickness.

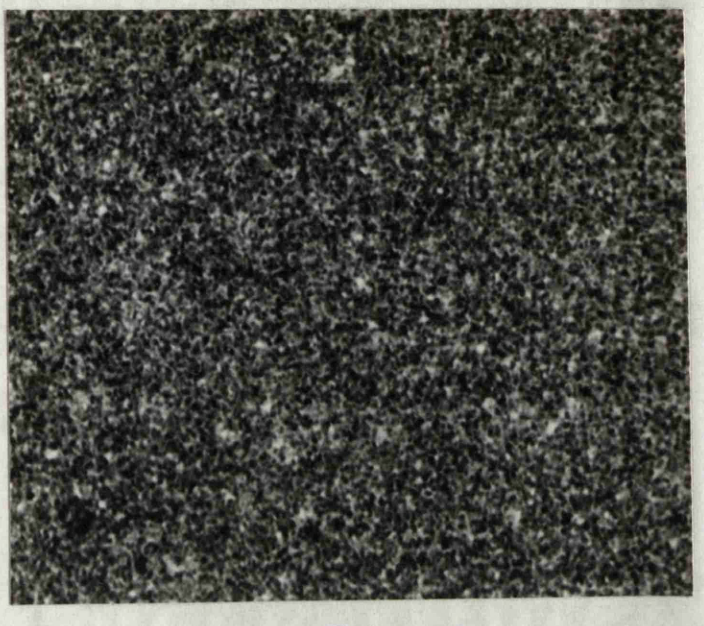
3. Results

In Chapter 7 it was found that the adhesion of metal films to glass could best be explained by dividing the metals into four broad groups. The film structure of several metals from each group has been examined with the following results.

Group 1

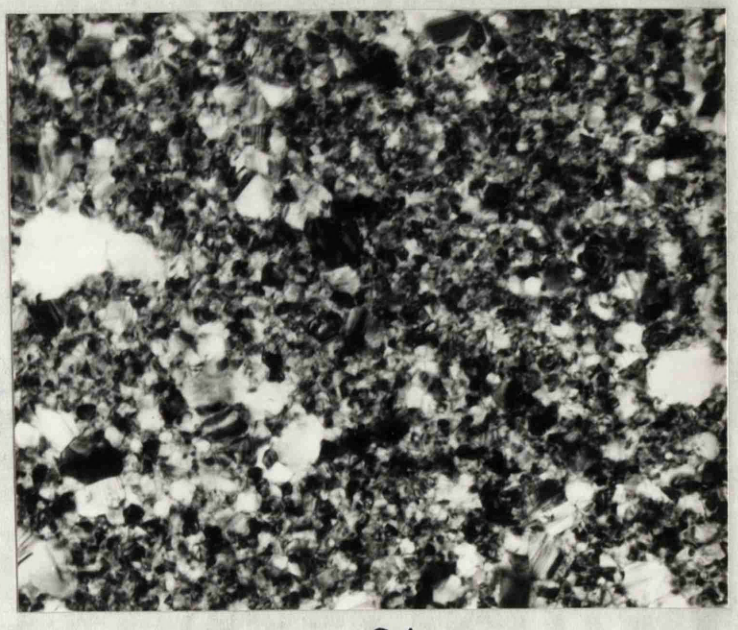
The film structure of all the metals in this group of Au, Ag and Cu, were examined. It can be seen from Plates 9.1 - 9.3 that the film structure of all these metals appears to be made up of a collection of separate crystallites of random shape and size. These crystallites can easily be detected in the case of the Ag film in Plate 9.2. Though the thickness of the film, measured by multiple-beam interferometry, is given as 200A, it can be seen that there is a large thickness range in the film from the very thin white areas to the thick dark areas. Definite crystal faces can be seen in the dark areas and this could mean that the crystallites have grown vertically by spiral growth from some suitable screw dislocation in the first layers of the film. A similar process could occur in the Au and Cu films. The average crystallite sizes for Ag, Cu and Au are approximately 600A, 200A and 100A respectively.

Electron diffraction showed that the crystallites in the film structure of these metals were face centred cubic and had the same lattice dimensions as the bulk metal. The diffraction pattern for the silver film is shown as an example in Plate 9.4 and it can be seen that there is no orientation of the crystallites.



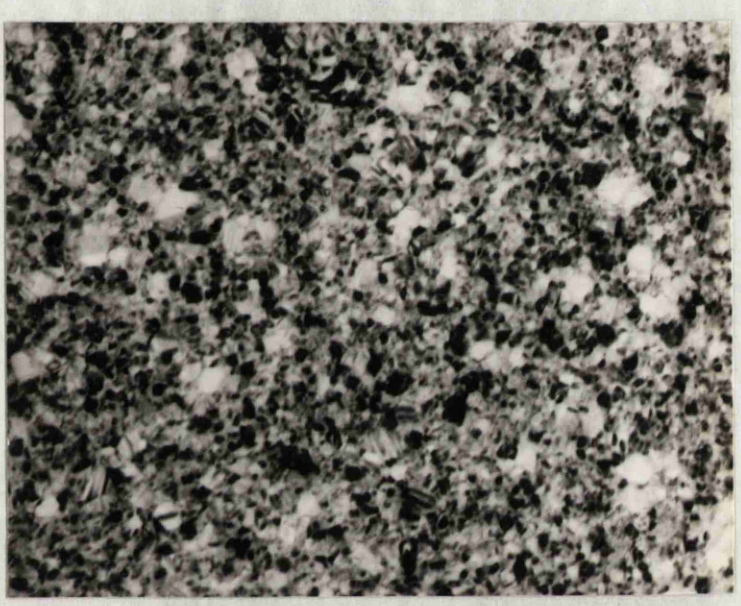
0.1μ

Plate 9.1. Electron micrograph of a gold film 150A thick. (x 47,500)



0.1μ

Plate 9.2. Electron micrograph of a silver film 200A thick. (x 83,000)



0.1μ

Plate 9.3. Electron micrograph of a copper film 200A thick. (x 83,000

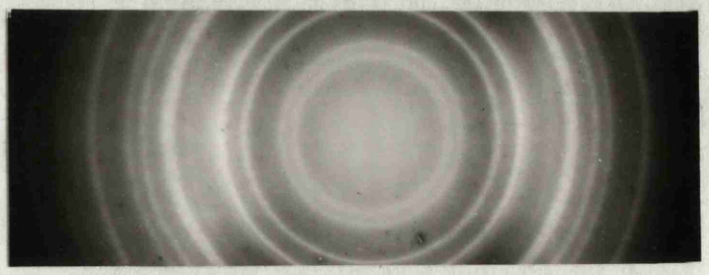
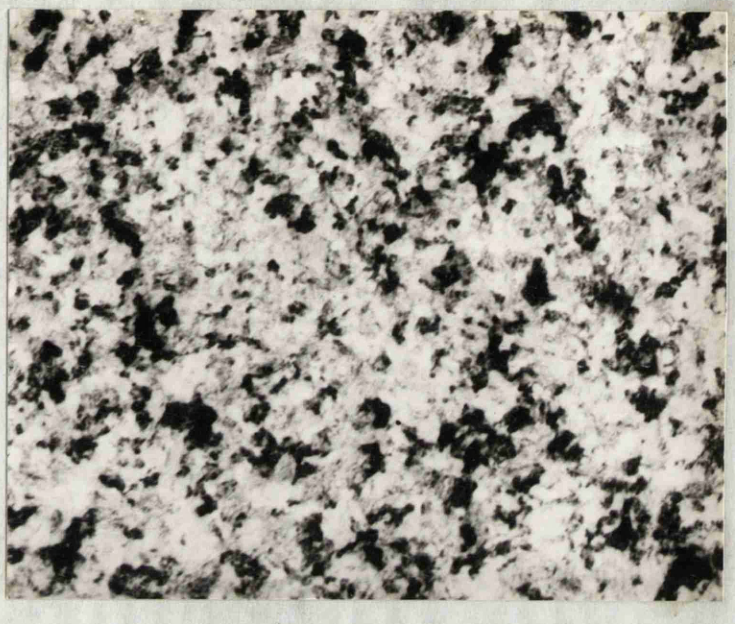


Plate 9.4. Electron diffraction pattern of silver film. Face centred cubic, a = 4.08AA.

Group 2

The film structures of Fe, Ni and Cr were examined by electron microscopy. The film structures of Fe and Ni are shown in Plates 9.5 and 9.6. These films have a continuous structure appearing to be a mozaic of very small grains. The grain sizes for Fe and Ni films are 600A and 100A respectively. Each of these grains may actually have originated from a single nucleus, the grain growing across the surface until a continuous film was formed. The grain boundaries can clearly be seen in the iron film. The regular shaped dark areas seen in the iron and nickel films may be due to the formation of fresh grains on the film surface, these grains being formed by vertical growth from suitable sites. The film structure of the Cr film is also continuous though, in this case, the fine structure appears to be made up of needles. A group of these needles is encircled (A) in Plate 9.7 and the size of a needle is approximately 100A long by 50A wide. This needle-like structure is similar to that of Martensite steel. Vertical growth of the film could again account for the dark areas observed in the structure. A large number of cracks can also be observed in the film structure, one of which is encircled (B), and the crack width is approximately 30A. The wavy nature of these cracks could indicate that they follow grain boundaries and it can be seen that the cracks



0.1μ

Plate 9.5. Electron micrograph of an iron film 200A thick. (x 83,000)

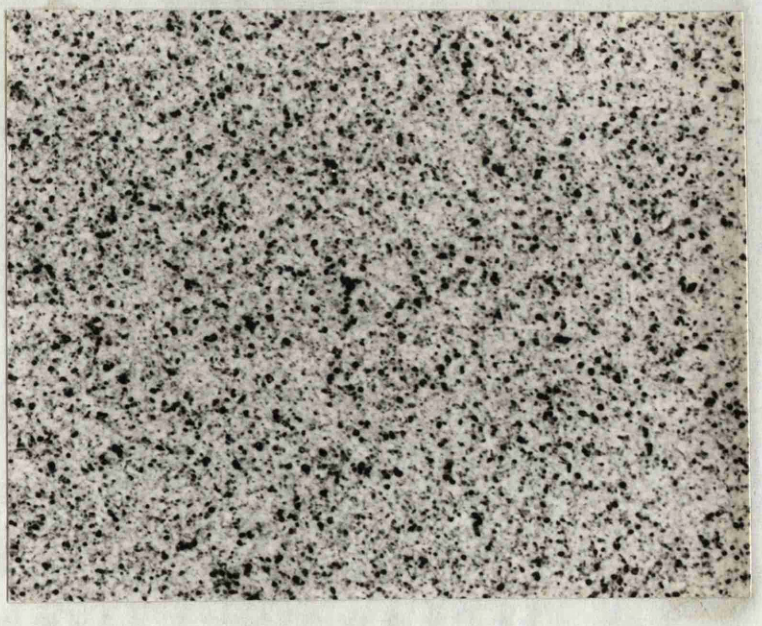


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Plate 9.6. Electron micrograph of a nickel film 100A thick. (x 81,000)

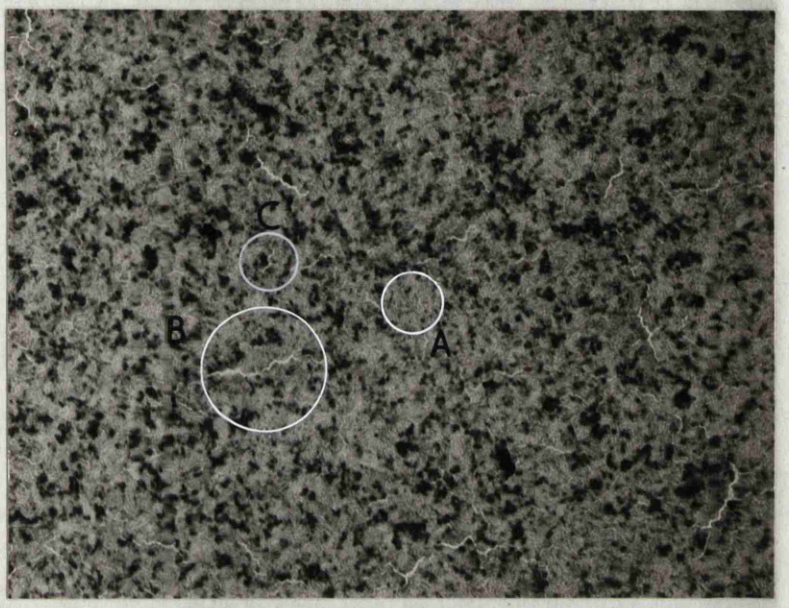


Plate 9.7. Electron micrograph of a chromium film 100A thick. (x 73,000)

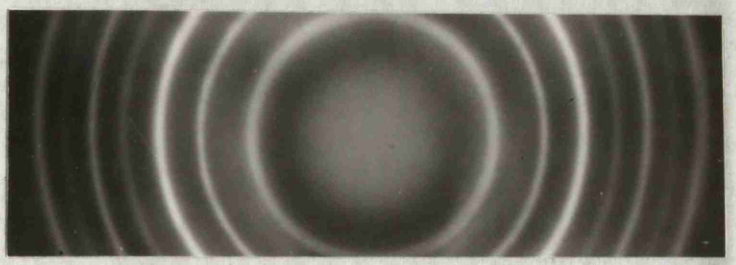


Plate 9.8. Electron diffraction pattern of a chromium film. Body centred cubic a = 2.88A

do go round the dark areas, as shown in circle (C). These cracks are presumably caused by stresses in the film structure but one can only postulate reasons for these stresses. The martensite structure found in steel is due to a very small percentage of impurity (0.2 - 0.8% Carbon) and it could be possible that there are residual impurities present in the Cr film which not only give this martensite type of structure but cause stresses to be set up in the film. On the other hand, chromium exhibits a phase change at 26°C., having an hexagonal structure below this temperature and a body centred cubic structure above. The electron diffraction pattern of the Cr film in Plate 9.8 indicates a body centred cubic structure with the lattice parameters of the bulk metal. Stresses could therefore be set up in the film as it tries to change its structure at this critical temperature.

Films of Fe, Ni, Mg and Ti were also examined by electron diffraction. The diffraction pattern for the Fe film indicated a body centred cubic structure which is the α phase. The pattern for the Ni film showed the structure to be face centred cubic which is the β phase. The lattice parameters for these two structures were the same as that for the bulk metals and there was no evidence of the presence of the oxide. However, the presence of oxide was observed

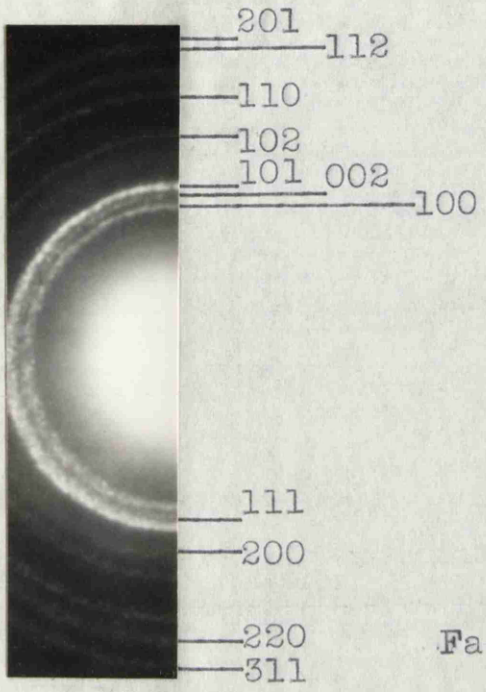
in the diffraction patterns of the Mg and Ti films. These patterns are shown in Plates 9.9 and 9.10 together with the lattice indices for each diffraction ring.

The diffraction patterns of Mo films were also examined but the films were not thick enough to give a sharp pattern which could be interpreted.

Group 3

The film structures of Zn and Cd of this group of low melting point metals were examined in the electron microscope. The structures, as shown in Plates 9.11 and 9.12, are quite different. The Zn film consists of semi-transparent plate-like crystals which tend to have a regular hexagonal shape and overlap one another. This crystal size is approximately 1000A. This is identical to the results of Sennett, McLauchlin and Scott[57]. On the other hand, the structure of the Cd film is a single layer of aggregates or islands of atoms of irregular shape and size separated by wide channels. The aggregates have a size of approximately 400A and the channels are of the order of 70A wide.

Films of Zn, Cd, Pb and Sn were examined by electron diffraction. The presence of oxide was observed in all the films. Plates 9.13 -9.16 show the full details of the structures of the metals and the oxides. It was found that the lattice parameters were the same as those of the



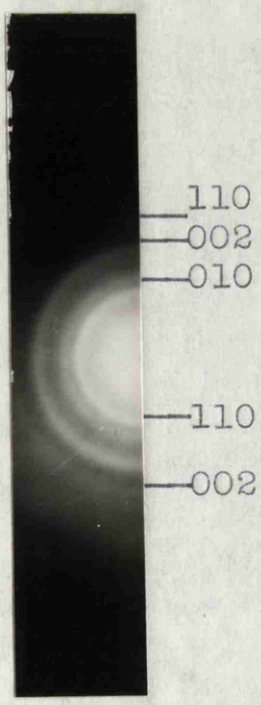
Magnesium

Hexagonal a = 3.20A
c = 5.20A

Magnesium oxide, MgO

Face centred cubic a = 4.21A

Plate 9.9. Electron diffraction pattern of a magnesium film.



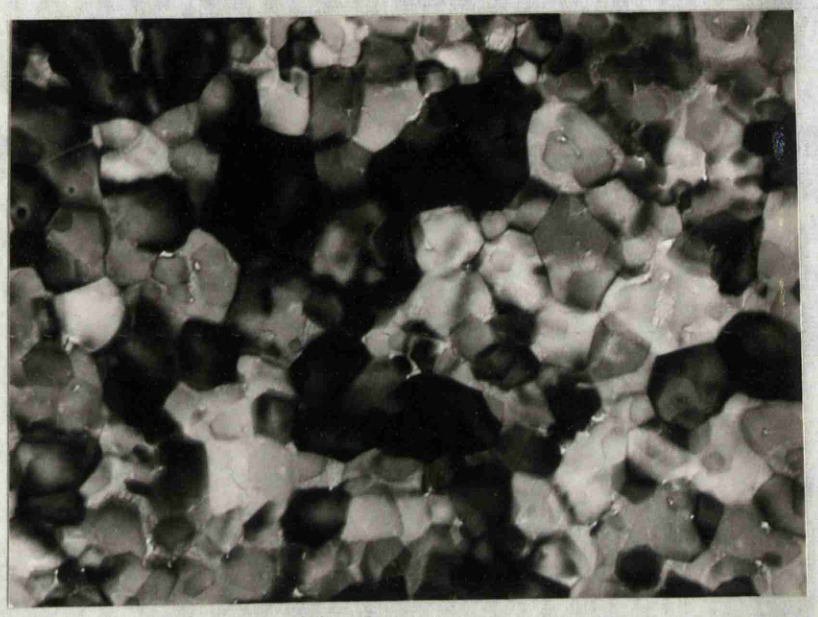
Titanium

Hexagonal a = 2.95A
c = 4.69A

Titanium dioxide (Rutile), TiO_2

Tetragonal a = 4.59A
c = 2.96A

Plate 9.10. Electron diffraction pattern of a titanium film.



0.1μ

Plate 9.11. Electron micrograph of a zinc film 250A thick. (x 72,000)

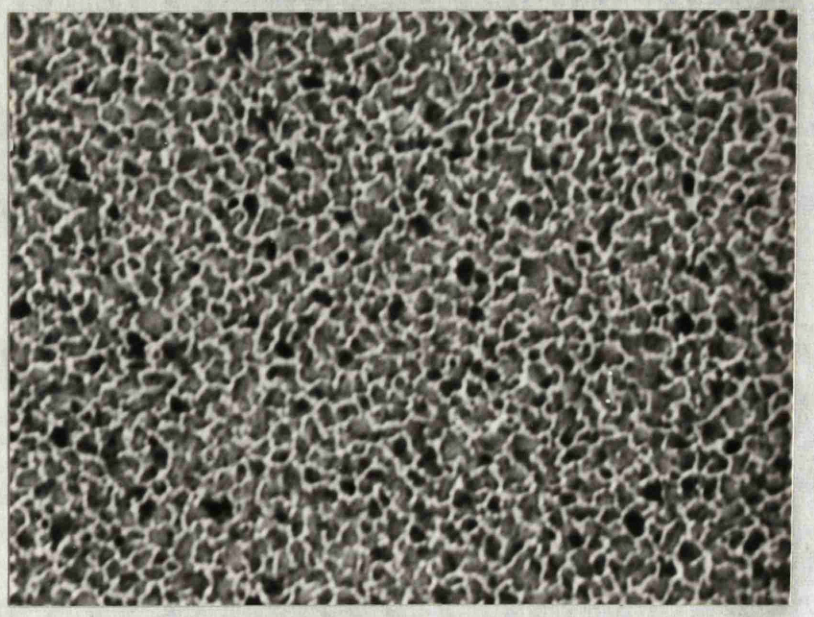


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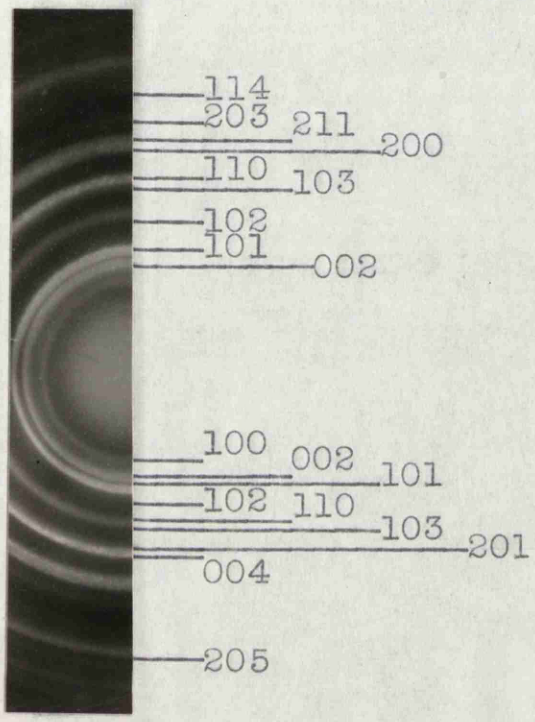
Plate 9.12. Electron micrograph of a cadmium film 100A thick. (x 72,000)



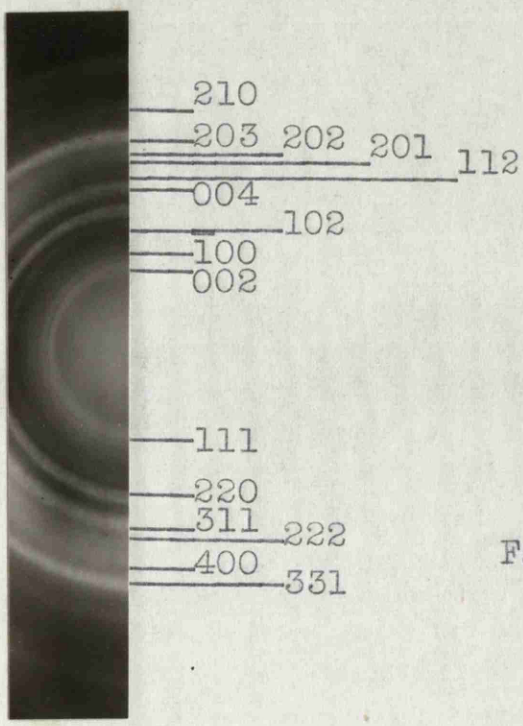
Zinc

Hexagonal a = 2.66A
c = 4.94A

Zinc oxide, ZnO

Hexagonal a = 3.25A
c = 5.21A

Plate 9.13. Electron diffraction pattern of a zinc film.



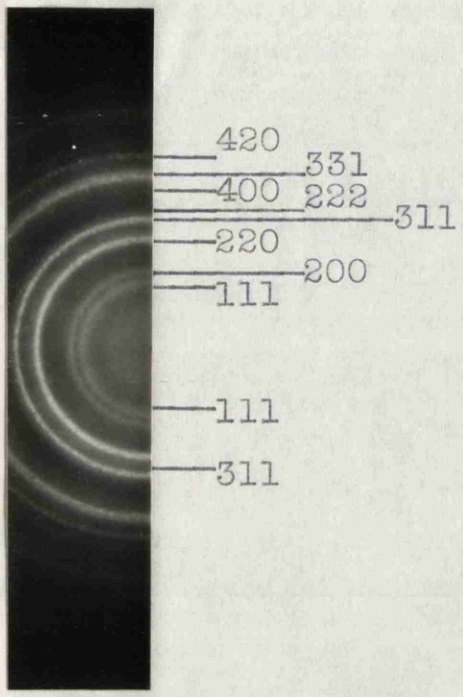
Cadmium

Hexagonal a = 2.97A
c = 5.61A

Cadmium oxide, CdO

Face centred cubic a = 4.70A

Plate 9.14. Electron diffraction pattern of a cadmium film.



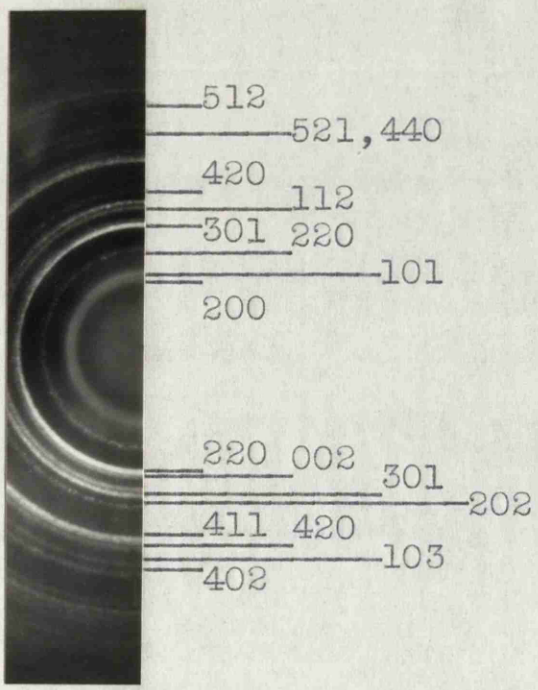
Lead

Face centred cubic a = 4.08A

Lead oxide (Yellow), PbO

Orthorhombic a = 5.49A
b = 4.76A
c = 5.89A

Plate 9.15. Electron diffraction pattern of a lead film.



Tin, β phase

Tetragonal a = 5.83A
c = 3.19A

Tin oxide, SnO_2

Tetragonal a = 4.74A
c = 3.19A

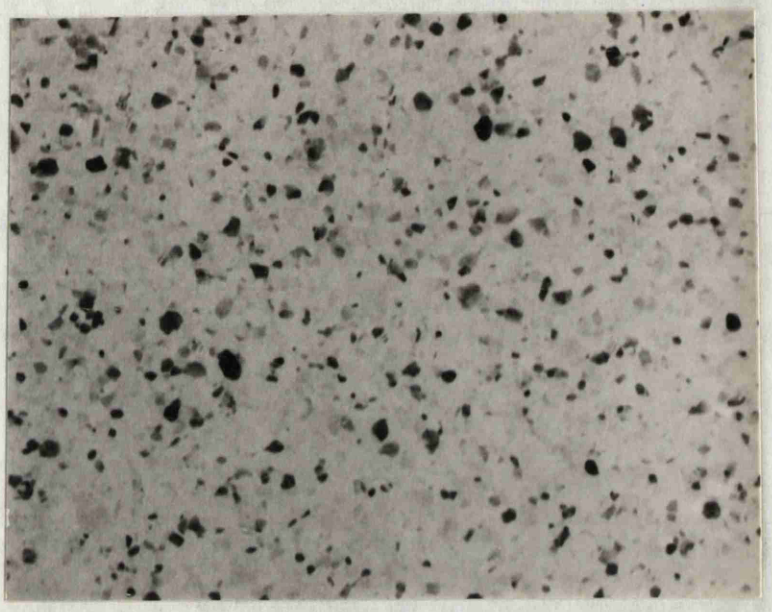
Plate 9.16. Electron diffraction pattern of a tin film.

bulk materials.

Group 4

The film structure of an aluminium film was examined and Plate 9.17 shows the continuous structure observed. There is no sign of aggregation or grain boundaries. Again the dark areas might be due to vertical growth of the film from suitable sites on the surface of the continuous structure. The electron diffraction pattern of this film, shown in Plate 9.18, indicates a face centred cubic structure with the lattice parameters of the bulk metal. There is no evidence of the presence of oxide.

The film structure of manganese could not be examined in detail since the film appeared to rupture the formvar substrate. This effect is shown in Plate 9.19 and it would seem that this is due to very great stresses in the film formed either during or after the deposition of the film. One possible reason for the presence of these stresses may be the tendency of the film to recrystallise, the breaking up of the film tearing the formvar substrate in the process. The diffraction pattern, shown in Plate 9.20, indicated the presence of the oxide MnO.



0.1μ

Plate 9.17. Electron micrograph of an aluminium film 150A thick. (x 73,350)

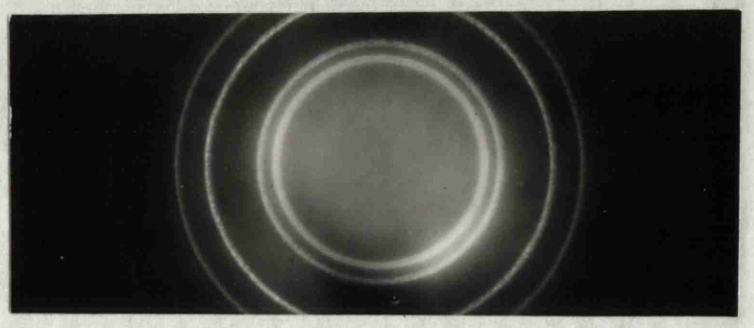
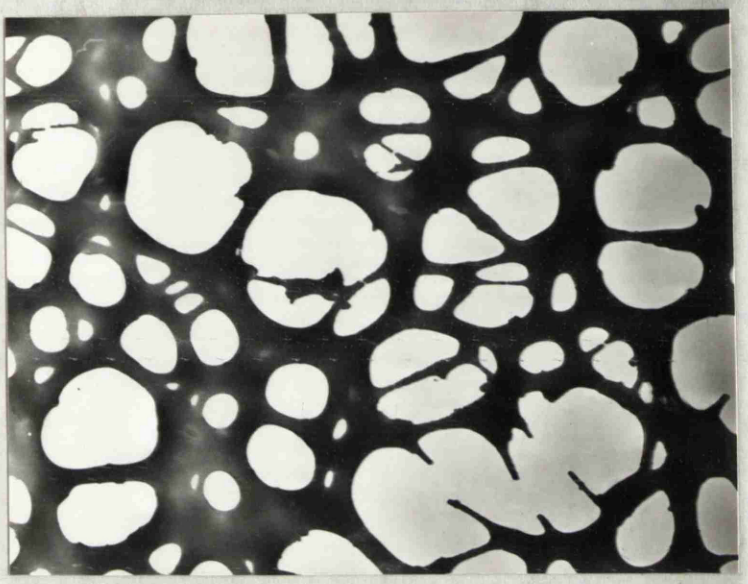
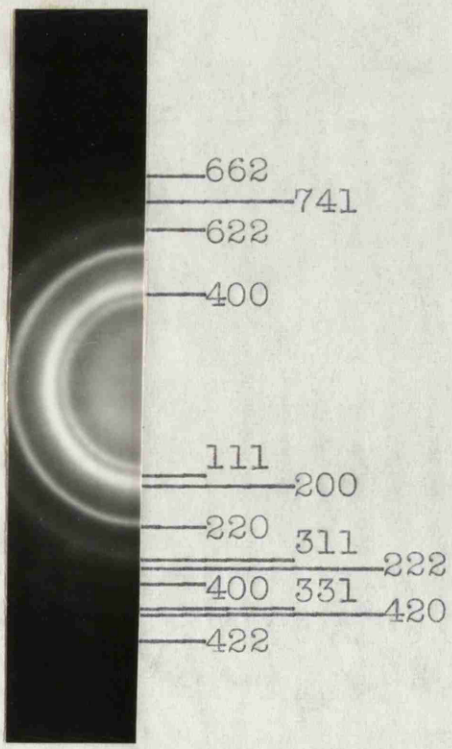


Plate 9.18. Electron diffraction pattern of an aluminium film. Face centred cubic, a = 4.04A



1 μ

Plate 9.19. Electron micrograph of a manganese film showing the rupture of the formvar substrate.
(x 8,000)



Manganese, α phase
Body centred cubic a = 8.89A

Manganese oxide, MnO
Face centred cubic a = 4.44A

Plate 9.20. Electron diffraction pattern of a manganese film.

4. Discussion

Films of Au, Ag and Cu all showed a similar structure of small crystallites. Mostovetch and Vodar[59] have stated that, where the film structure is aggregated, gas could readily be adsorbed by the film. The open film structures of the metals in this group would certainly permit the adsorption of gas and this could account for the rapid rise in adhesion observed with a number of Cu films. Oxygen from this adsorbed gas, reacting with the copper, could assist in the formation of an intermediate copper oxide layer at the metal-glass interface, the adhesion rising as the layer is built up and becoming constant when the layer is completed. The adhesion of gold and silver films would not be affected by the adsorption of gas since the affinity of these metals for oxygen is much poorer.

The continuous structure of fine grains and needles observed in Fe, Ni and Cr films support the assumptions made when discussing the adhesion of these films to glass. It was suggested that the rise in adhesion with time for these films could be due to the diffusion of oxygen along grain boundaries to the metal-glass interface to complete the formation of an intermediate layer of oxide. These grain boundaries are actually observed in Fe and Ni films and their presence in Cr films could be inferred by the nature

of the cracks observed. The cracks themselves would also provide paths for the oxygen to reach the interface.

The oxide observed in Mg and Ti films could have been formed in the film structure during the deposition of the film or it could have grown on the film surface afterwards. It is very difficult to obtain the metals Mg and Ti in the raw state free from oxide and the evaporation of these metals with a large oxide content may, to some extent, account for the presence of the oxide in the film structure. The structure observed for MgO was face centred cubic which is the structure of the bulk material and similar to the results of Stahl[17]. However, Finch and Quarrell[60] have shown that the oxide formed on the surface of magnesium exposed to air had an hexagonal structure. This could indicate that the oxide observed in the present investigation was formed within the film structure. If the oxide was formed in the first layers of the film as it built up then this layer could account for the strong adhesion observed immediately after deposition of the films on glass. Similarly, the strong adhesion of Ti to glass may indicate that the oxide observed was formed at the metal-glass interface.

It was suggested in Chapter 7 that the poor adhesion observed with the low melting point metals was due

to their highly aggregated film structure. This aggregated structure has been verified in the cases of Zn and Cd. The structure of the Zn film appeared to consist of layers of regular shaped crystals. These crystals would have very little cohesion between themselves and would slide over each other easily. There would only be a few of these crystals in contact with the glass surface so that the adhesion of the film as a whole would be very poor. The structure of the Cd film is different to that of Zn. In this case, the atoms build up in randomly shaped aggregates separated by wide channels. However, each of these aggregates is in contact with the substrate surface and this would account for the stronger adhesion observed with Cd films on glass.

Both the Zn and the Cd type of structure would readily adsorb gas molecules and, though the adhesion of the films would not be affected, this adsorption could account for the presence of the oxide observed in Zn, Cd, Pb and Sn films.

Aluminium films were shown to have a continuous structure with no sign of aggregation or grain boundaries. The diffraction pattern showed no evidence of the oxide. This could account for the poor adhesion observed with aluminium films on glass. If the aluminium film was deposited as a continuous structure with only a small number of oxygen molecules trapped in the structure then these

molecules would require a large activation energy to diffuse through the lattice. These molecules would therefore take time to diffuse to the interface where there would be a slow build up of oxygen. This build up may have to reach a certain level before the adhesion is affected. This would account for the poor initial adhesion and the sudden rise in adhesion after approximately 200 hours. It is well known that aluminium forms a protective oxide coating on itself. The formation of such a coating on the film surface immediately after deposition of the film would prevent oxygen from the atmosphere entering the film structure and therefore only the oxygen trapped during deposition would affect the adhesion of the film. This could mean that the intermediate oxide layer at the metal-glass interface may only be partially formed and the final adhesion would be low.

It was suggested that recrystallisation of the manganese film after deposition caused the rupturing of the formvar substrate. Recrystallisation could also explain the variation of adhesion with time observed with Mn films on glass. If the Mn film was deposited as a continuous structure with no intermediate oxide layer formed then the initial adhesion would be poor. However, if the film recrystallised then gas could be adsorbed from the atmosphere and there could be a reaction at the interface to form an

oxide layer. This would give the rise in adhesion observed after 150 hours. Electron diffraction has shown the presence of the oxide.

5. Conclusions

This investigation has given evidence in support of the assumptions made as to the role played by the film structure in explaining the adhesion of metal films to glass.

In iron, nickel and chromium films, where the film structure was continuous but the adhesion rose rapidly to very high values, grain boundaries and cracks were observed which would allow the passage of oxygen molecules through the structure to the metal-glass interface. However, in the case of aluminium, which also had a continuous film structure, there was no sign of any grain boundaries or discontinuities in the structure which would permit the passage of oxygen molecules through the structure. Due to the formation of a protective oxide layer on the film surface after deposition, only oxygen trapped in the film structure could diffuse to the metal-glass interface and this lattice diffusion would be slow. This could explain the poor initial adhesion of these films, the sudden rise in the adhesion after approximately 200 hours being due to an accumulation of the slowly diffusing molecules at the

interface. The poor initial adhesion of manganese films could be due to a similar structure though the rise in adhesion after 150 hours is, in this case, due to recrystallisation of the film allowing gas to enter the structure.

The highly aggregated structure observed in zinc and cadmium films supports the assumption made earlier that the poor adhesion of the low melting point metals was due to this type of structure.

CHAPTER 10

ELECTRICAL PROPERTIES OF THIN METALLIC FILMS

1. Introduction

The electrical properties of a thin film are very closely related to the film structure as well as to the film thickness. In fact, due to the film structure, electrical conduction may only become apparent when the film has reached an appreciable thickness. At this stage the film will have a specific resistivity many times greater than the value for the bulk material. As the film thickness increases, the resistivity tends to approach the bulk value. However, in some cases the resistivity may remain greater than the bulk value and this could indicate the presence of impurities, occluded gases, or a highly aggregated structure. The changes in resistance with time after deposition also give an indication of structural changes occurring within the film.

Since it has been suggested that the film structure plays an important role in the adhesion of a film to a glass surface, it was decided to examine the resistance of the films in conjunction with the adhesion measurements. Therefore

a sample of the metal film being deposited for the adhesion measurements was collected on a separate glass slide in the form of a thin strip between two silver electrodes, which had been previously fired on to the surface. The dimensions of the strip were approximately 6.5 cm. x 0.2 cm. and this gave a range of resistance of 5 - 10,000 ohms, depending upon the film material and its thickness. The specific resistivity of the film can be calculated as follows:-

$$\text{Specific resistivity} = R. \frac{W}{L} . t \quad \text{ohms.cm.}$$

where R = resistance of the metal strip (ohms)

W = width of strip (cm.)

L = length of strip (cm.)

and t = film thickness (cm.)

2. Measurement of Resistance

After deposition the specimens were removed from the chamber and the D.C. resistance measured by a simple Wheatstone Bridge arrangement. A Post Office box was used both for the ratio and the balancing arms, the box having been checked to be in standard ohms. A two volt storage cell supplied the necessary voltage through a 62 K ohms resistor and a Pye galvanometer with a sensitivity of 700 mm./uA was used for balancing the bridge. The specimen

was held on a wooden board by two massive brass blocks clamped over the silver electrodes. The contact resistance between the brass clamps and the silver electrodes was found to be only a fraction of an ohm.

In the measurement of D.C. resistances of films other than silver, it was thought that a contact potential might be present between the film and the silver electrode, in which case the resistance measured would be too high. By varying the voltage across the bridge, the presence of a contact potential would be indicated by a variation in the resistance of the film. Tests were carried out on specimens of a number of metals, the voltage across the bridge being varied from 0.1 mV to 200 mV. In all cases there was no change in the resistance of the films measured at these voltages, indicating that there was no contact potential present between the film and the silver contact. As a further check, an A.C. bridge was used since, with this type of bridge, a contact potential would be eliminated. The resistances of the films measured over a frequency range of 50 c/s to 20 Kc/s showed no appreciable variation and were in good agreement with corresponding values of the D.C. resistances.

3. Results

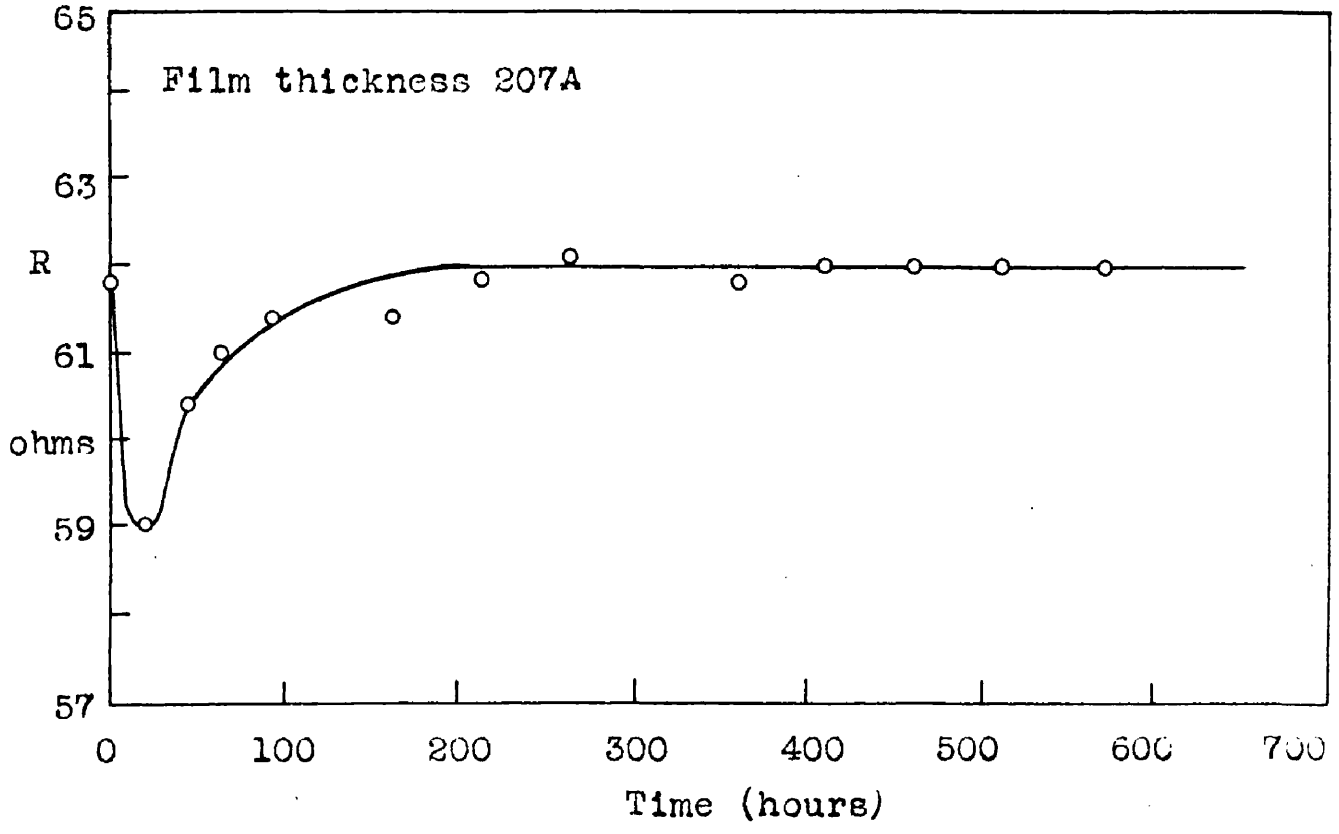
Since the resistance of the films was only measured after the specimens had been removed from the chamber, there was a time lapse of about three minutes between deposition of the film and the first resistance measurement. As mentioned in Chapter 7, there was a similar time lapse before the first adhesion measurement was made.

Once again the results are best described by taking the metals in groups, as previously suggested.

Group 1

Figures 10.1 - 10.3 show the variation of resistance with time for films of Au, Ag and Cu. Au and Cu films showed an initial drop in resistance but, while the resistance of Cu films then remained constant, the resistance of Au films rose slightly with time. This initial drop in resistance was only observed with thick Ag films ($>$ 300A), the thinner films showing a steady rise in resistance over the whole time period.

The initial specific resistivities were calculated for each specimen using the initial value of the resistance. It was found that the resistivities of Au, Ag and Cu films became constant at a film thickness of approximately 300A at



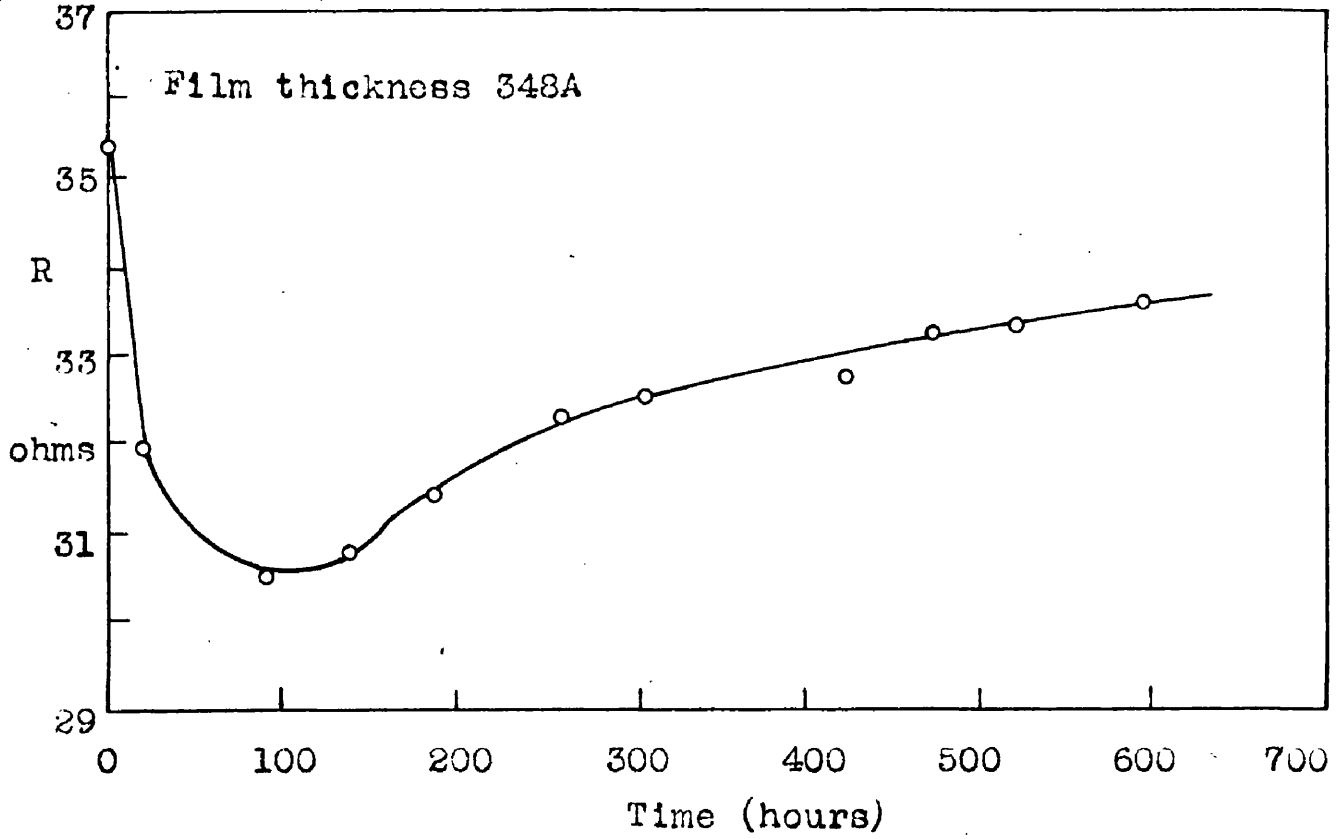


Figure 10.1. Variation of resistance (R) with time for GOLD films on glass.

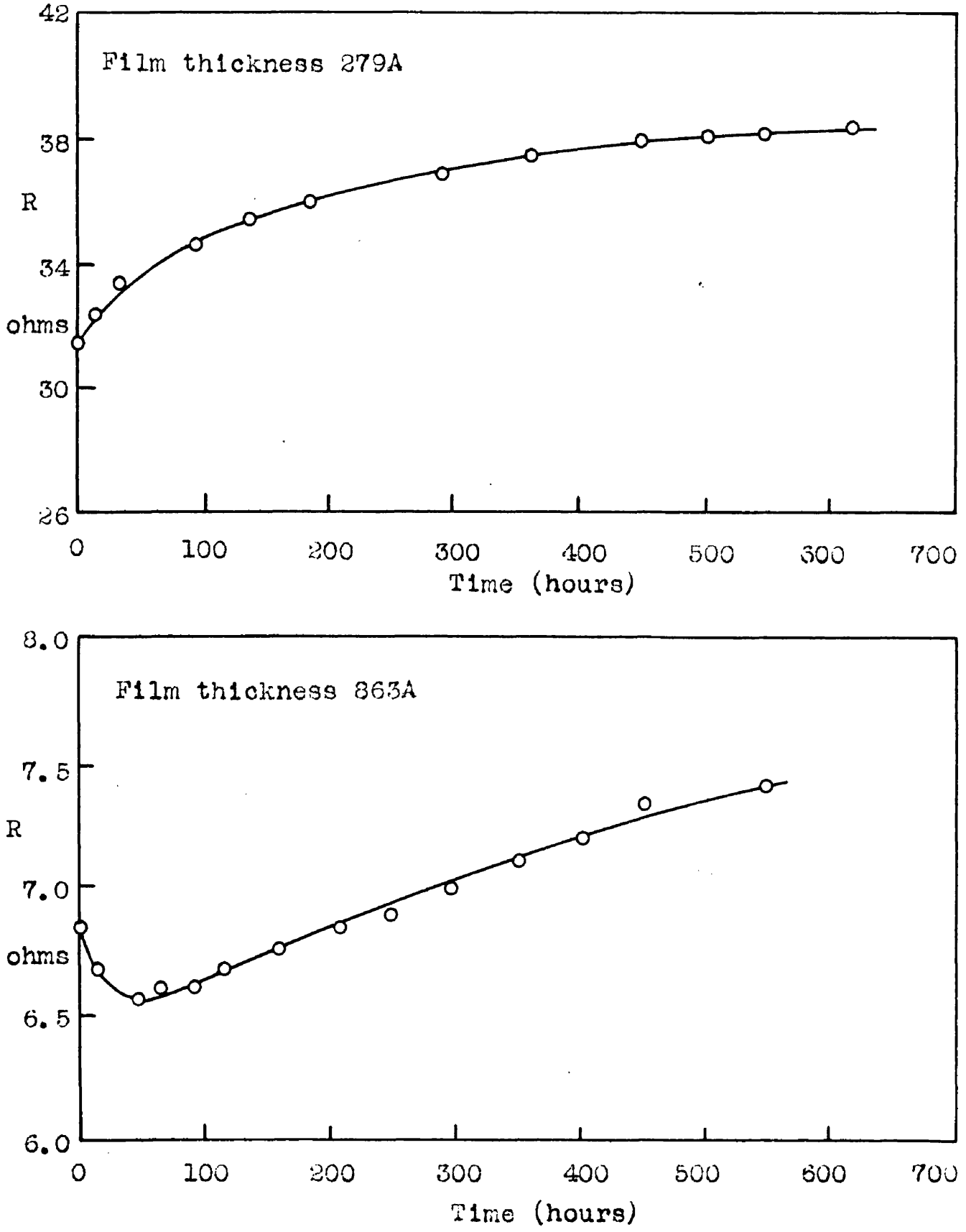
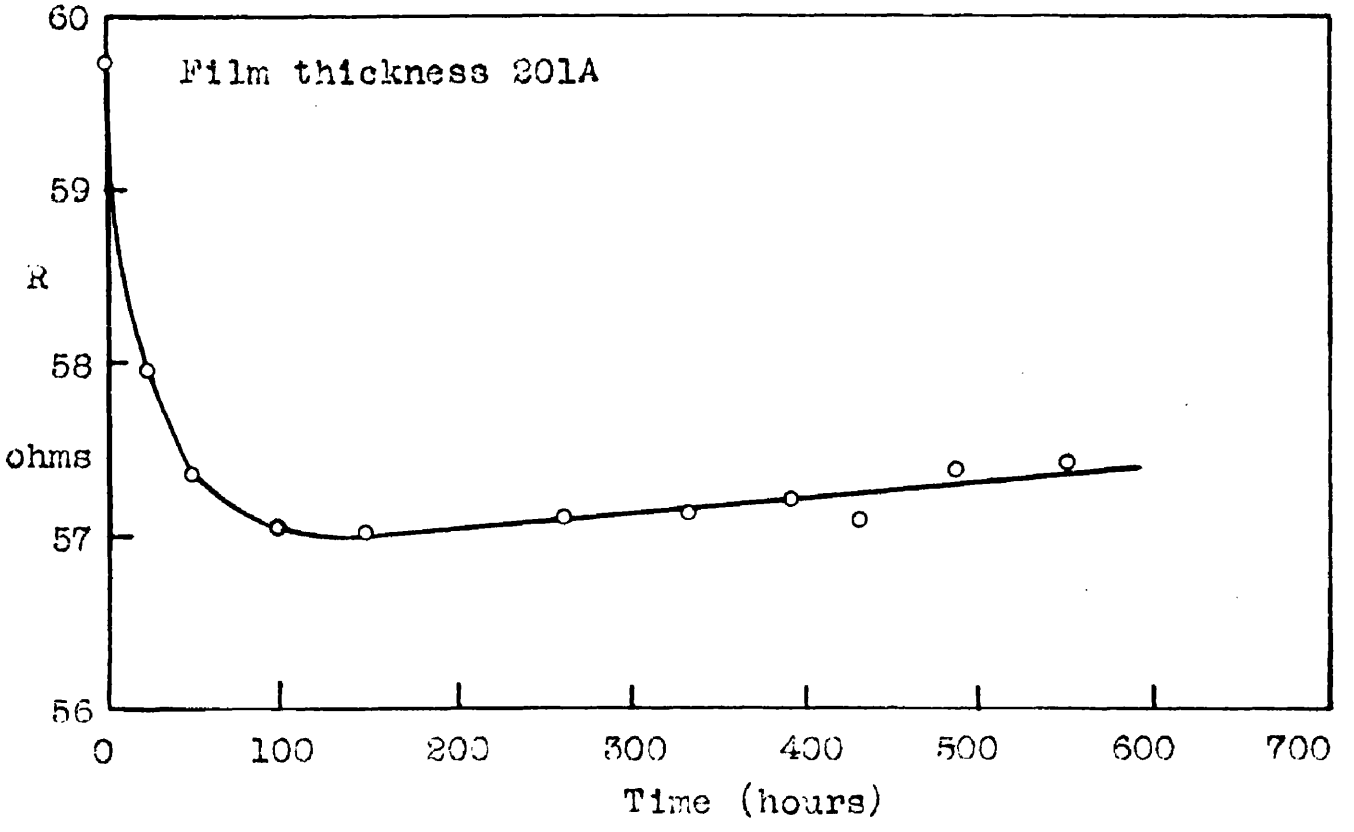


Figure 10.2. Variation of resistance (R) with time for SILVER films on glass.



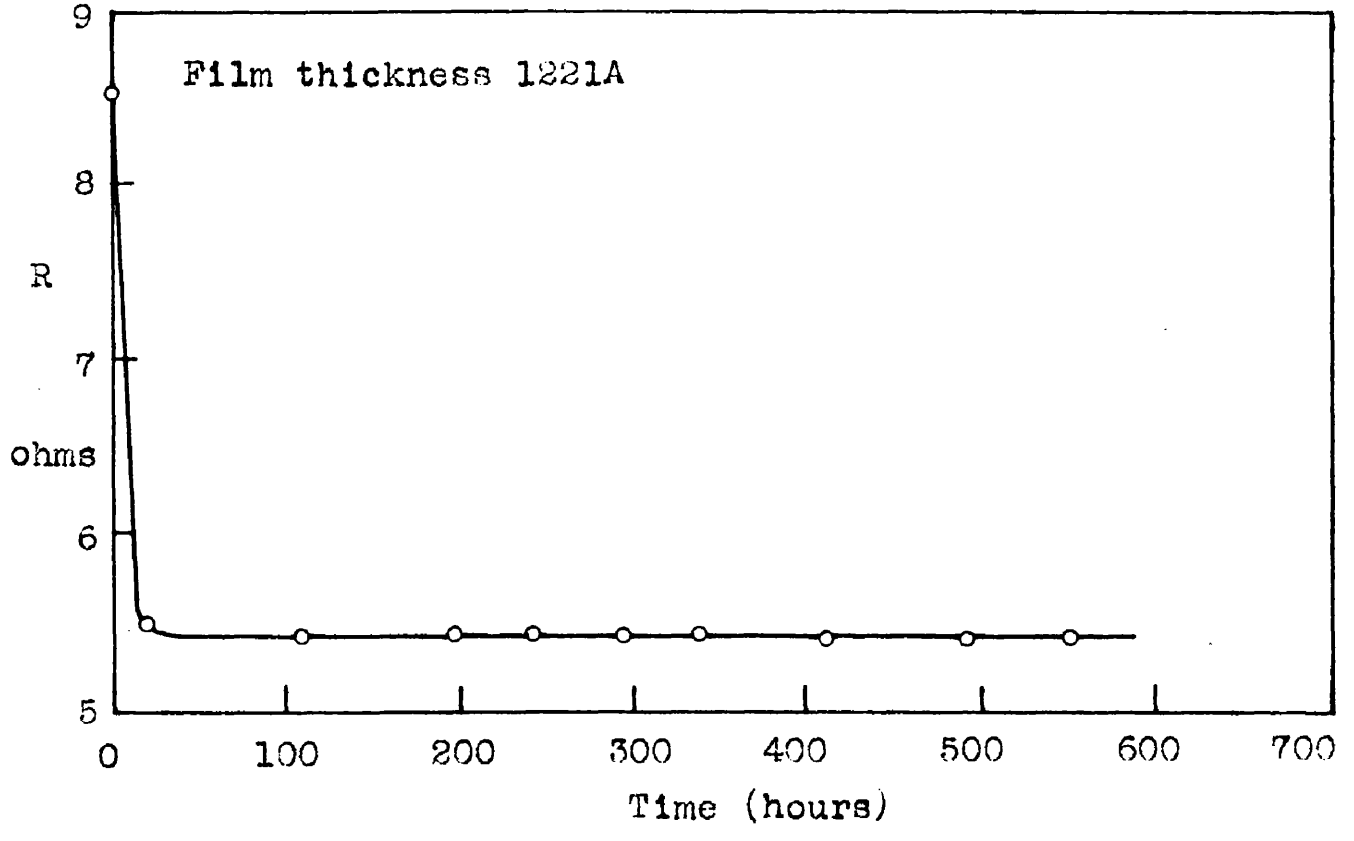


Figure 10.3. Variation of resistance (R) with time for COPPER films on glass.

values slightly greater than the values for the bulk materials.

Group 2

The metals in this group were Ni, Mo, Fe, Cr, Ti, Zr and Mg. Films of Zr and Mg examined either had an infinite resistance or had a very high initial resistance which rapidly became infinite. In the case of Mg, this appeared to be due to breakdown of the film at the silver electrodes. For Zr films, the infinite resistances were probably due to the thinness of the films. However, the variation in resistance with time observed with films of Ni, Mo, Fe, Cr and Ti are shown in Figures 10.4 - 10.8. Films of Ni, Mo and Fe showed a steady rise in resistance with time whereas the resistance of Cr and Ti films, after an initial rise, became fairly constant.

The initial specific resistivities of films of these metals were found to be several times greater than the bulk values. This was understandable in the cases of Ni, Mo and Ti, where only thin films were examined. However, in the cases of Cr and Fe, a wide range of film thickness was examined and, even so, the resistivities approached constant values which were still high. Figure 10.9 shows the experimental values of the initial specific resistivity plotted against thickness for chromium films. It can be

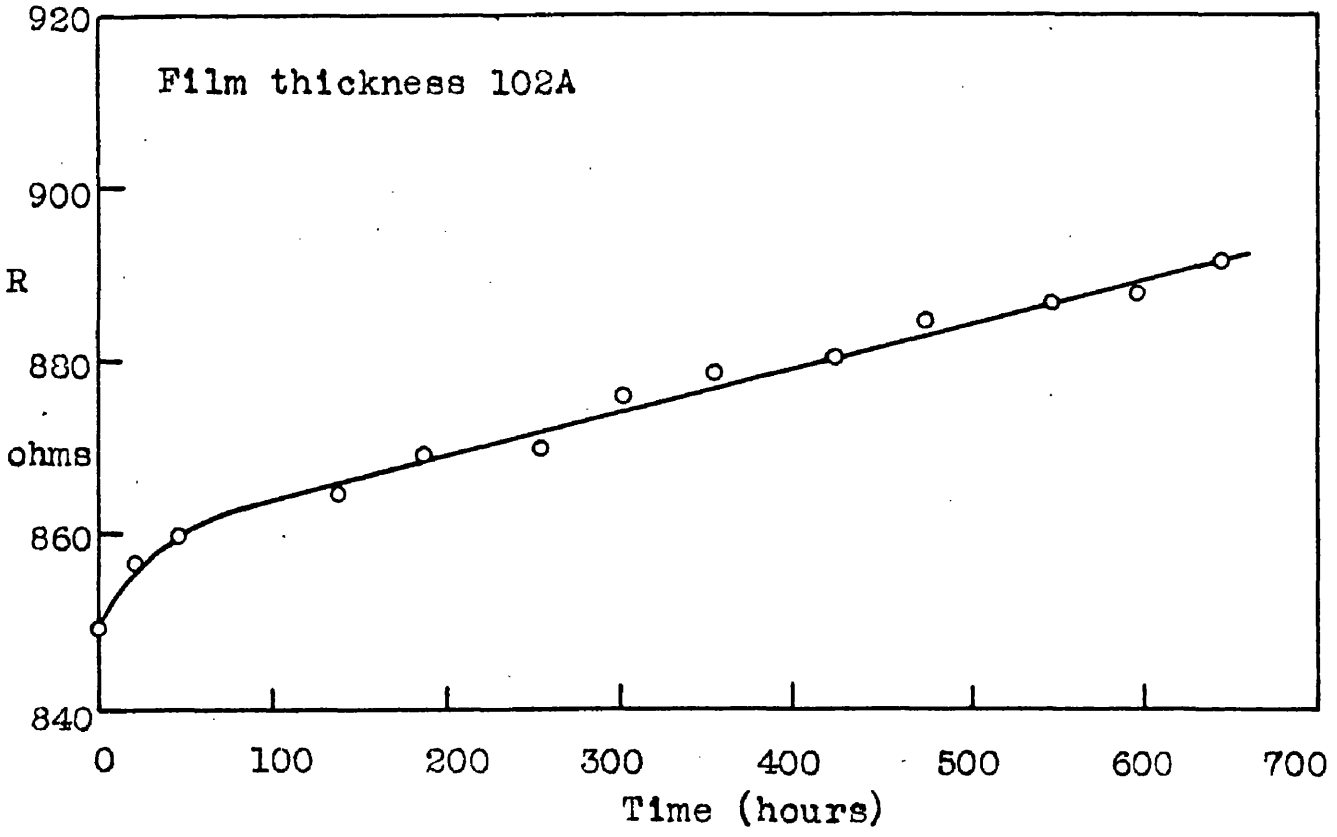


Figure 10.4. Variation of resistance (R) with time for NICKEL films on glass.

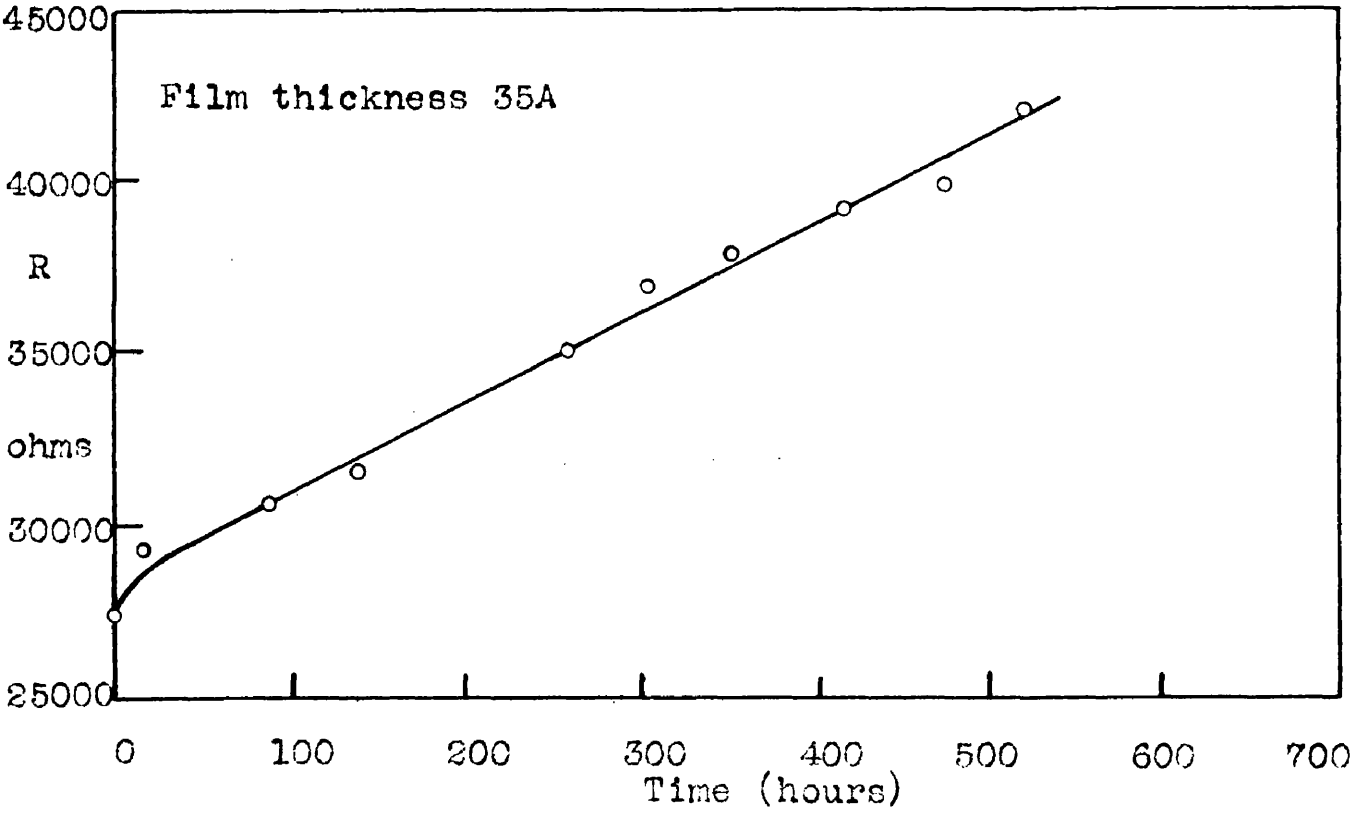
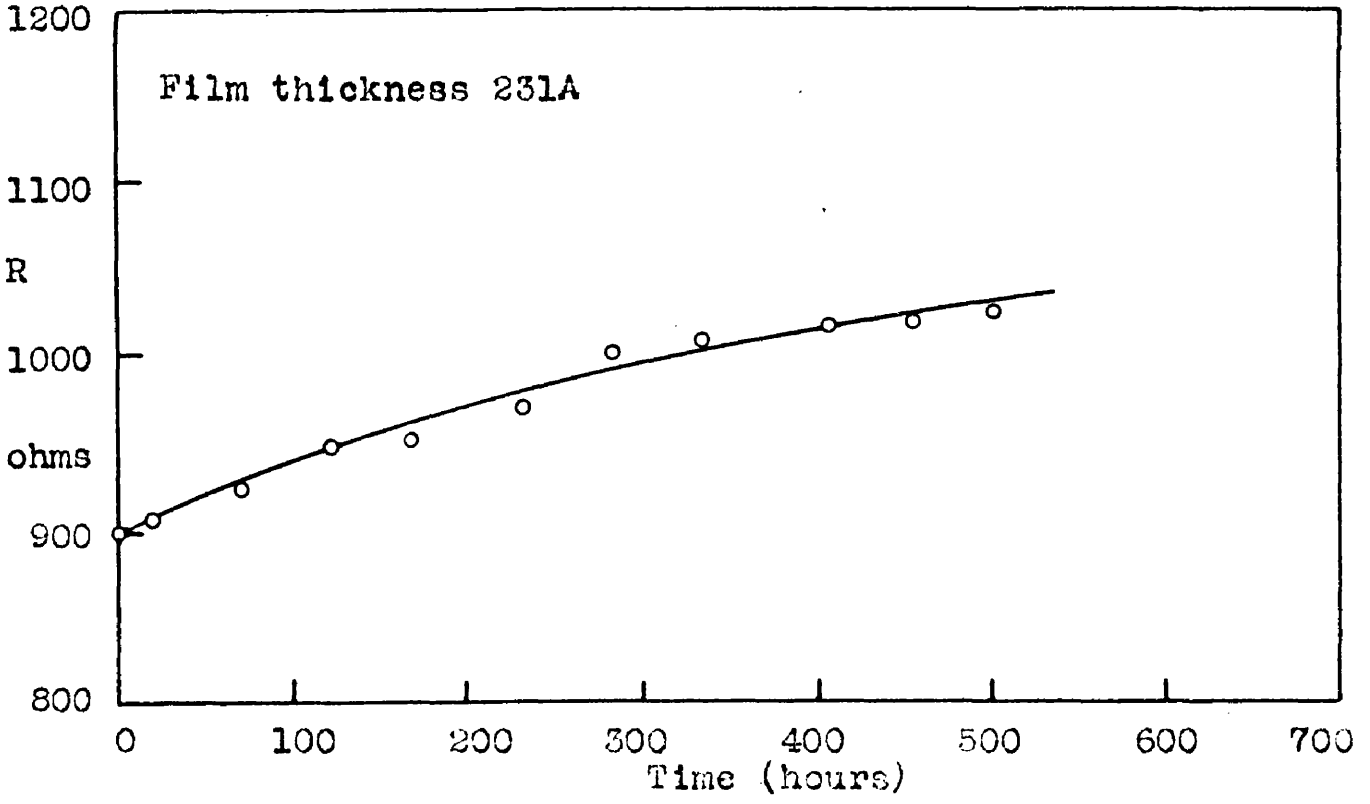


Figure 10.5. Variation of resistance (R) with time for MOLYBDENUM films on glass.



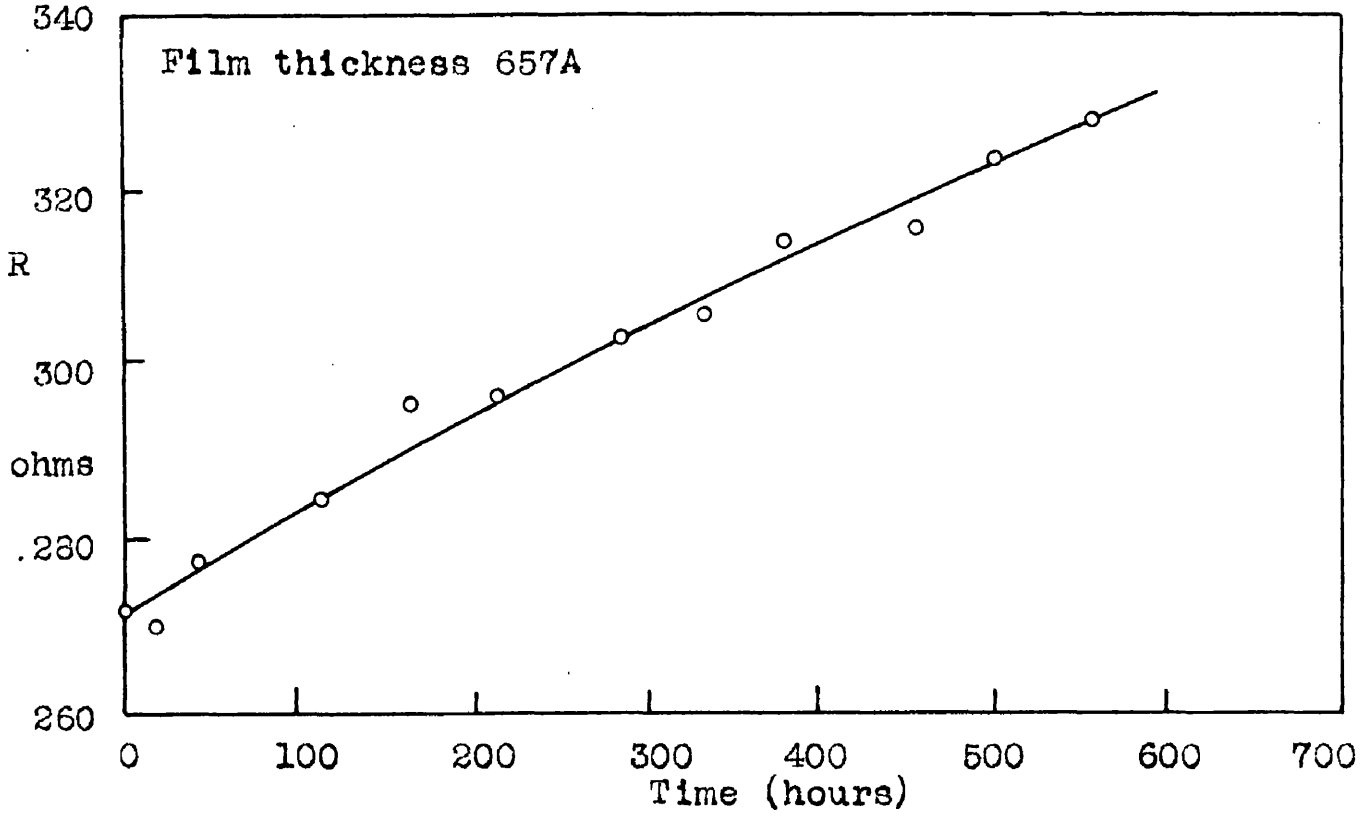
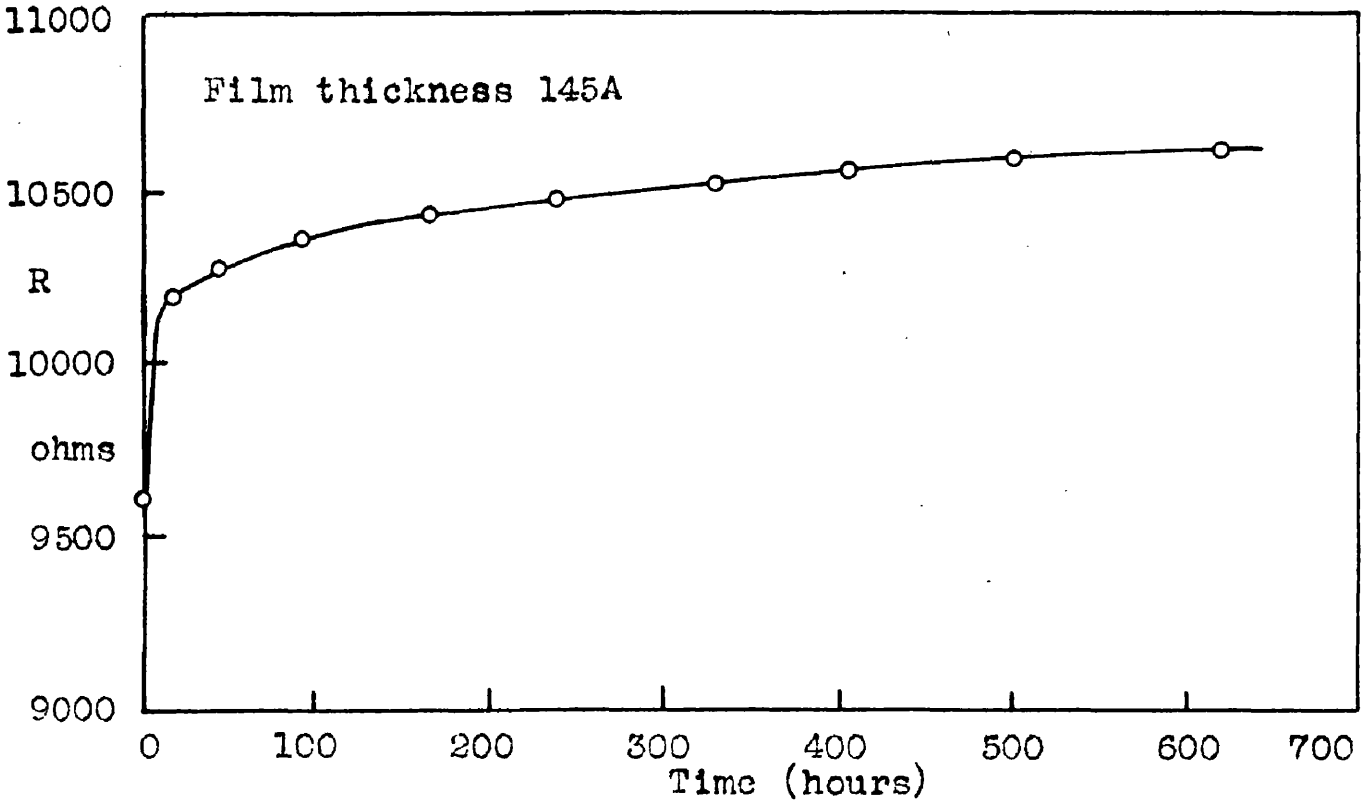


Figure 10.6. Variation of resistance (R) with time for IRON films on glass.



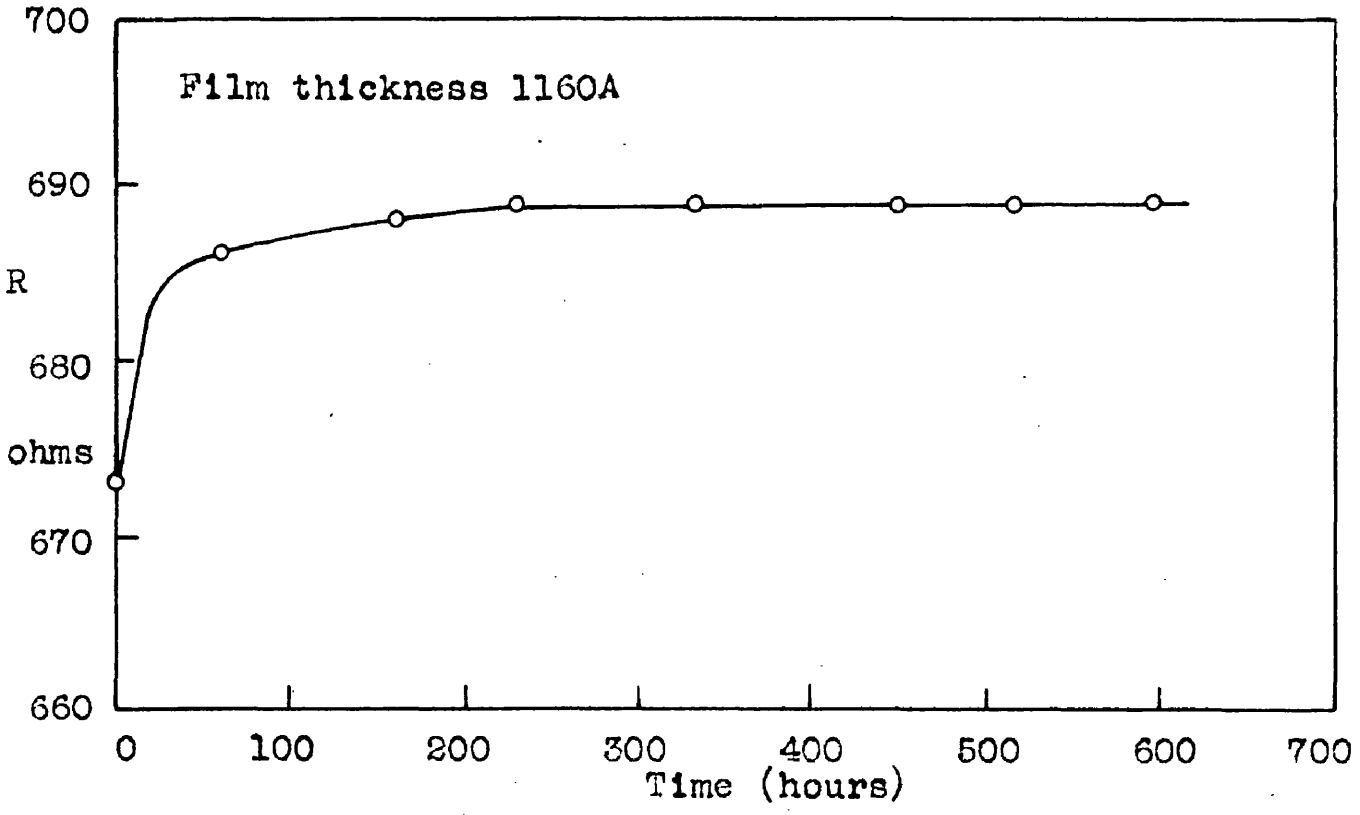


Figure 10.7. Variation of resistance (R) with time for CHROMIUM films on glass.

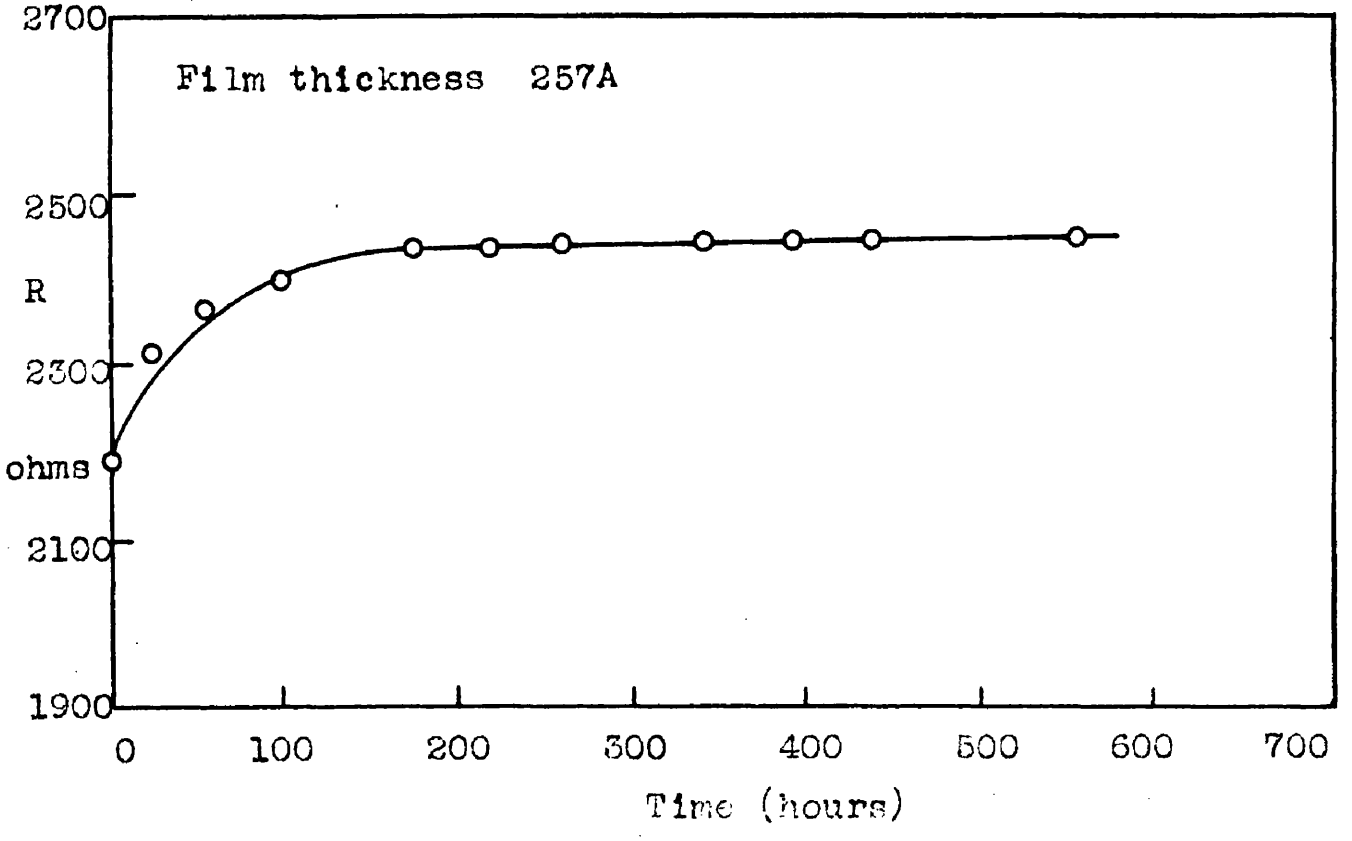


Figure 10.8. Variation of resistance (R) with time for TITANIUM films on glass.

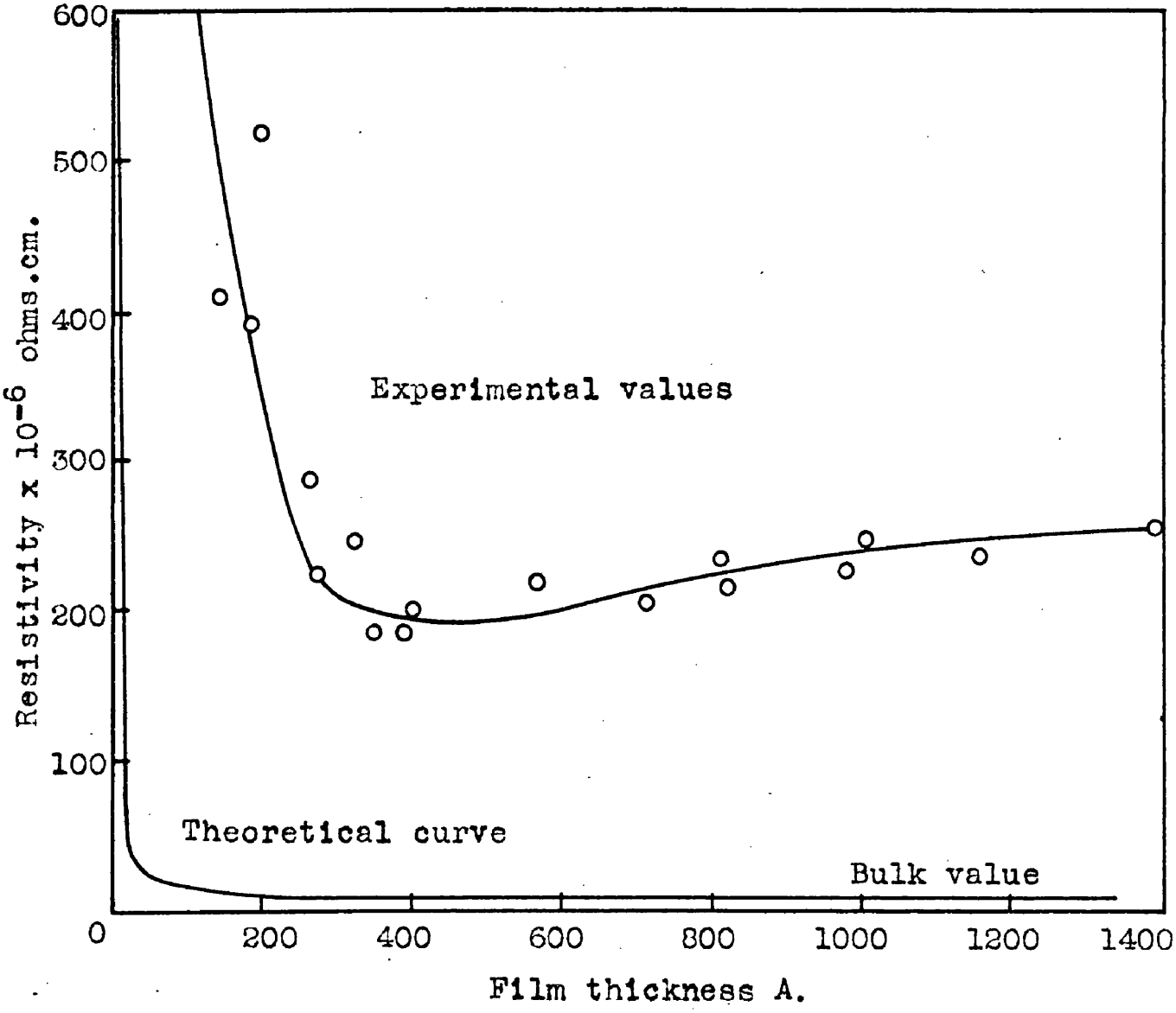


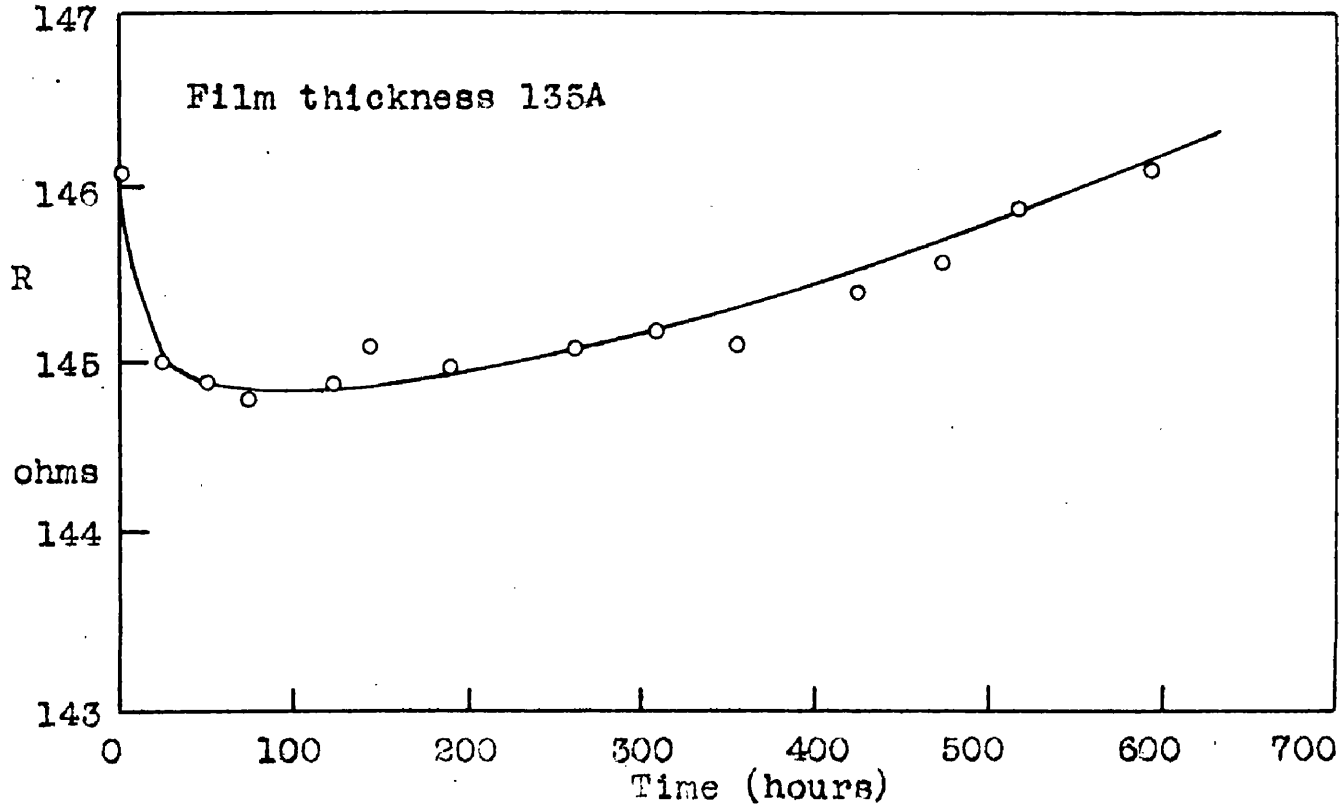
Figure 10.9. Resistivity versus film thickness for CHROMIUM films.

seen that the resistivity drops rapidly as the thickness increases until, at approximately 400A, there is a rise in the resistivity to a fairly constant value which is about twenty times greater than the bulk value. Also shown in Figure 10.9 is the theoretical curve of resistivity for Cr films over the same thickness range calculated from Fuchs[61]. Fuchs' theory considers that the films are homogeneous and only takes into account the boundary effects due to film thickness. The theoretical curve shown was calculated assuming that all the conduction electrons were randomdly reflected from the boundaries of the film and that the mean free path of these electrons was 500A. Comparing this theoretical curve with the experimental values it can be seen that there is a large discrepancy between theory and experiment which is probably due to the effect of film structure.

Group 3

The variations of resistance with time for films of this group of low melting point metals are shown in Figures 10.10 - 10.13. It can be seen that for films of Cd, Pb and Sn, the resistance either showed a slight increase with time or remained fairly constant. Films of Zn showed a slight initial drop in resistance followed by a steady rise.

The initial specific resistivities of these metal



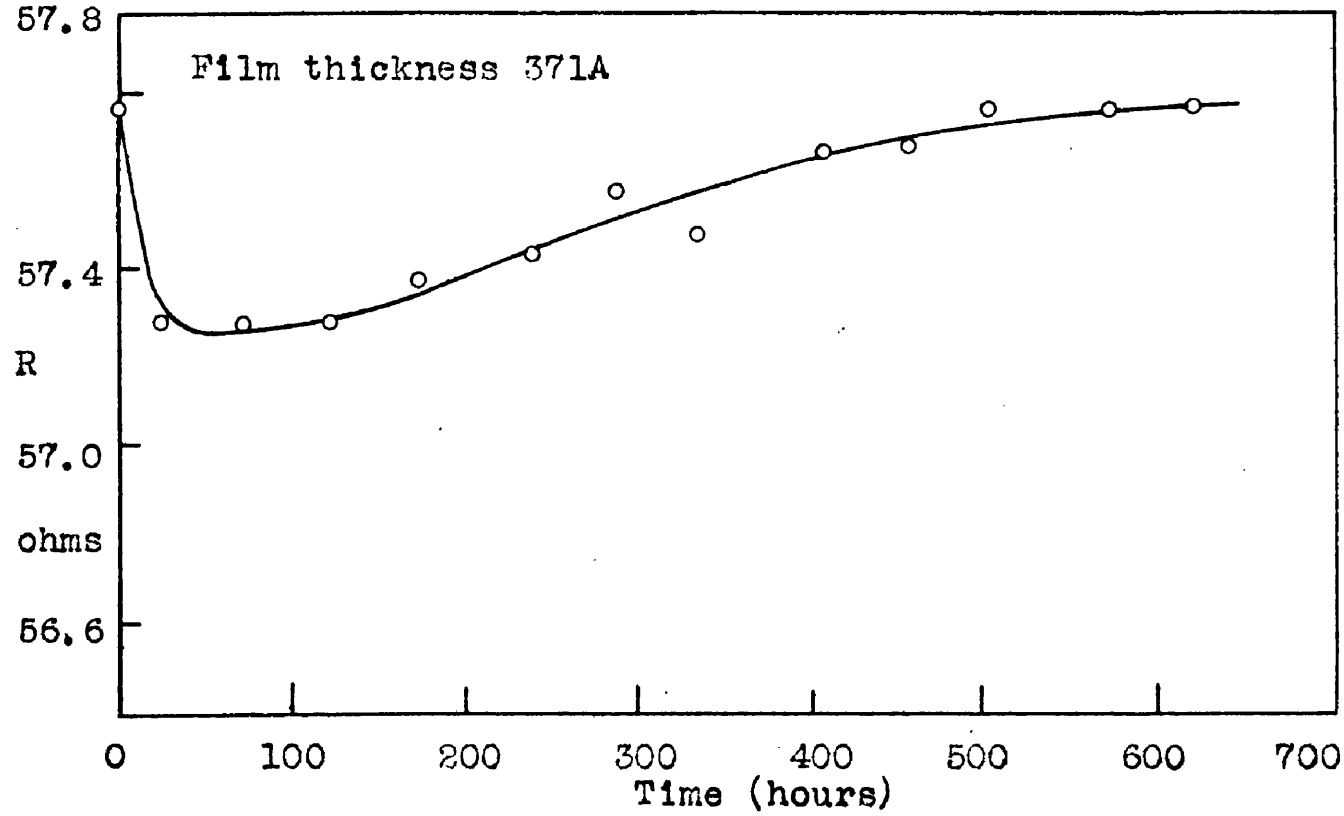


Figure 10.10. Variation of resistance (R) with time for ZINC films on glass.

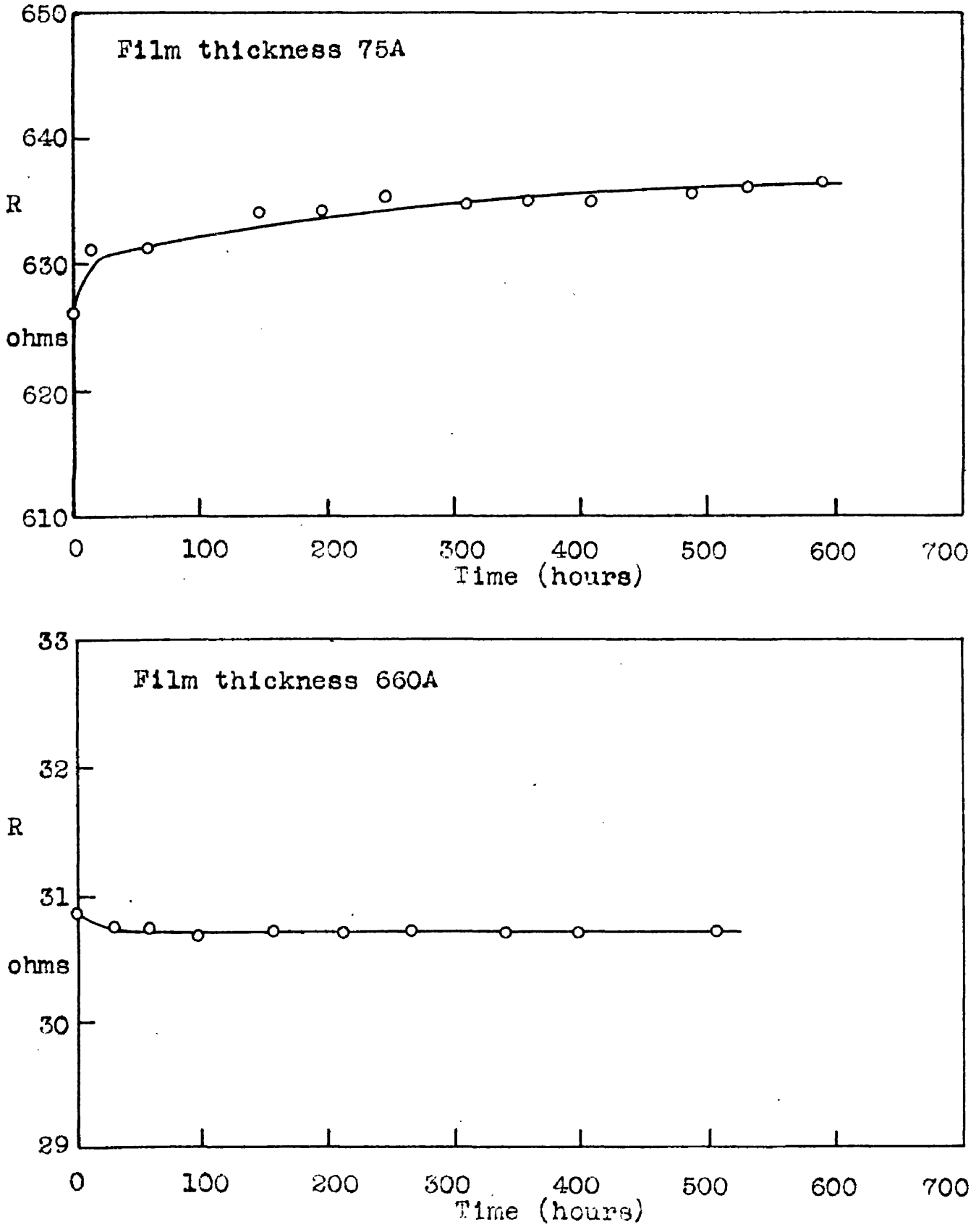


Figure 10.11. Variation of resistance (R) with time for CADMIUM films on glass.

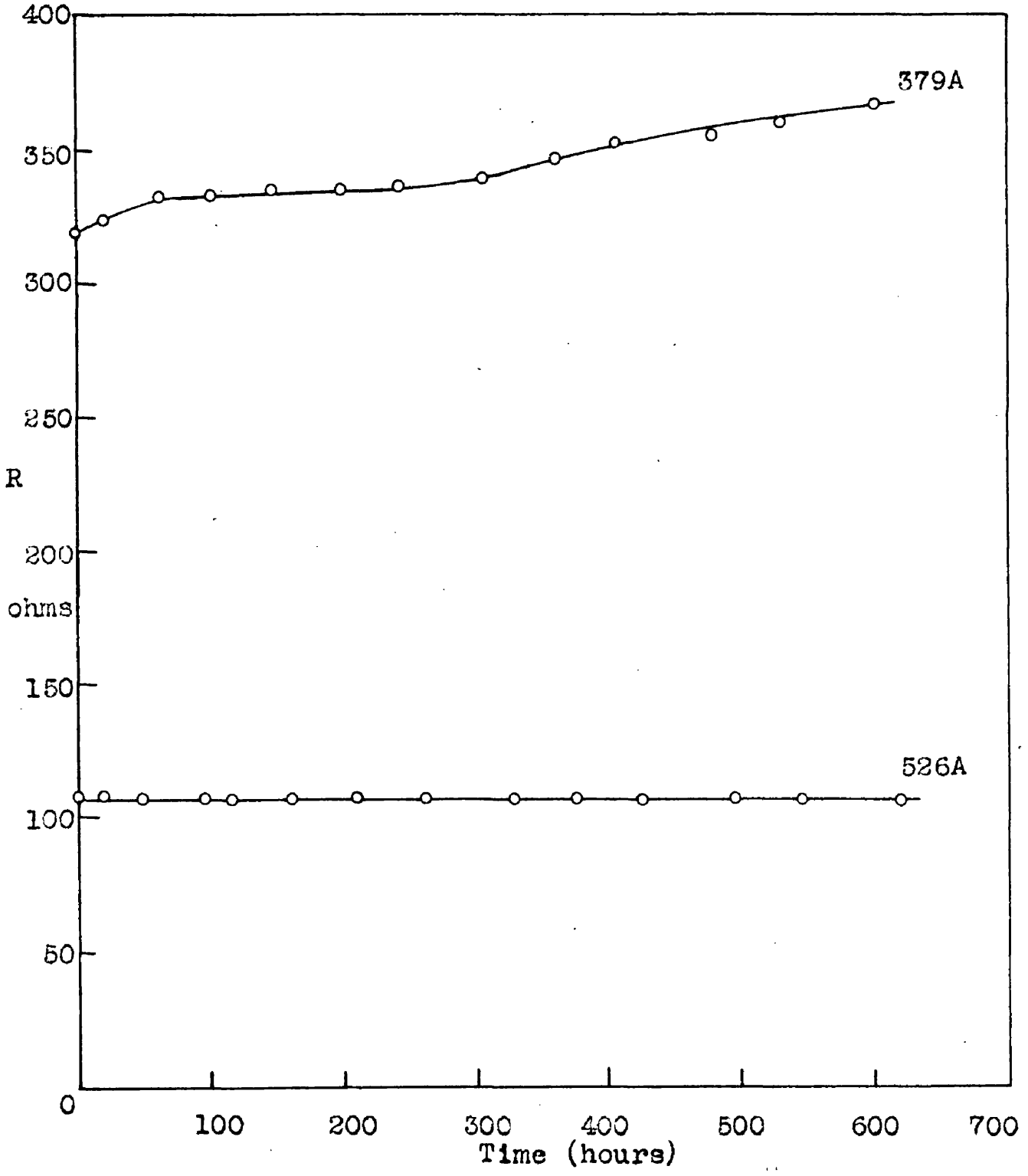


Figure 10.12. Variation of resistance (R) with time for LEAD films on glass.

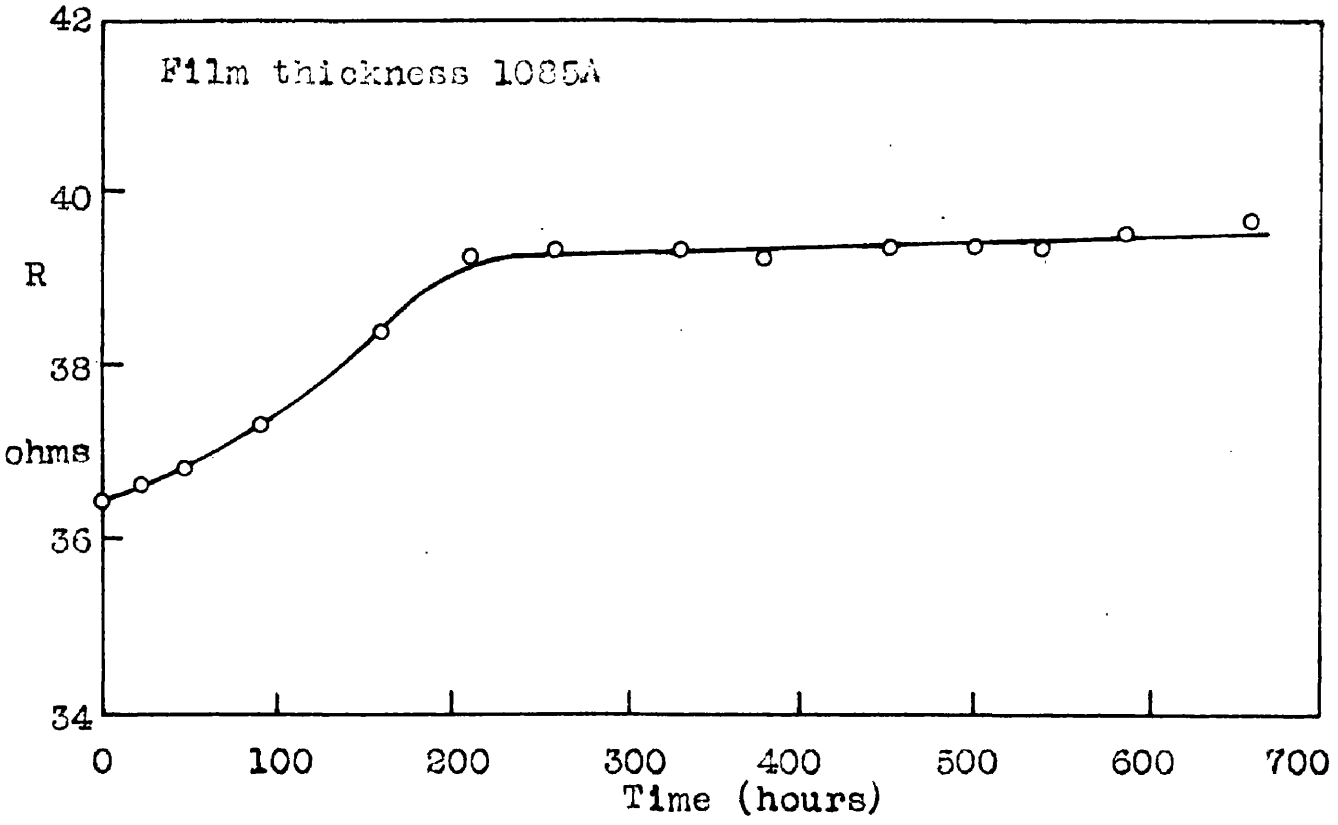


Figure 10.13. Variation of resistance (R) with time for TIN films on glass.

films approached a constant value slightly higher than those of the bulk metals as the film thickness was increased.

Group 4

The variation of resistance with time for aluminium films is shown in Figure 10.14 and it can be seen that there is an initial rise in resistance but that a continuous value is soon reached. The theoretical values of the resistivity for aluminium films were again calculated after the theory of Fuchs[61], assuming that all the conduction electrons are randomly reflected from the boundaries of the film and have a mean free path of 500A. These values are shown in Figure 10.15 together with the experimental values of the initial specific resistivities. It can be seen that there is very good agreement between the theoretical and experimental values. The slight discrepancy at very small film thicknesses could be due to errors in the measurement of thicknesses of the order of 50-100A.

The variation of resistance with time for Mn films is shown in Figure 10.16. Again, there is an initial rise in the resistance but, instead of becoming constant, there is a further rise in resistance at approximately 150 hours. The resistance only then becomes constant. The initial specific resistivities were actually lower than the bulk values.

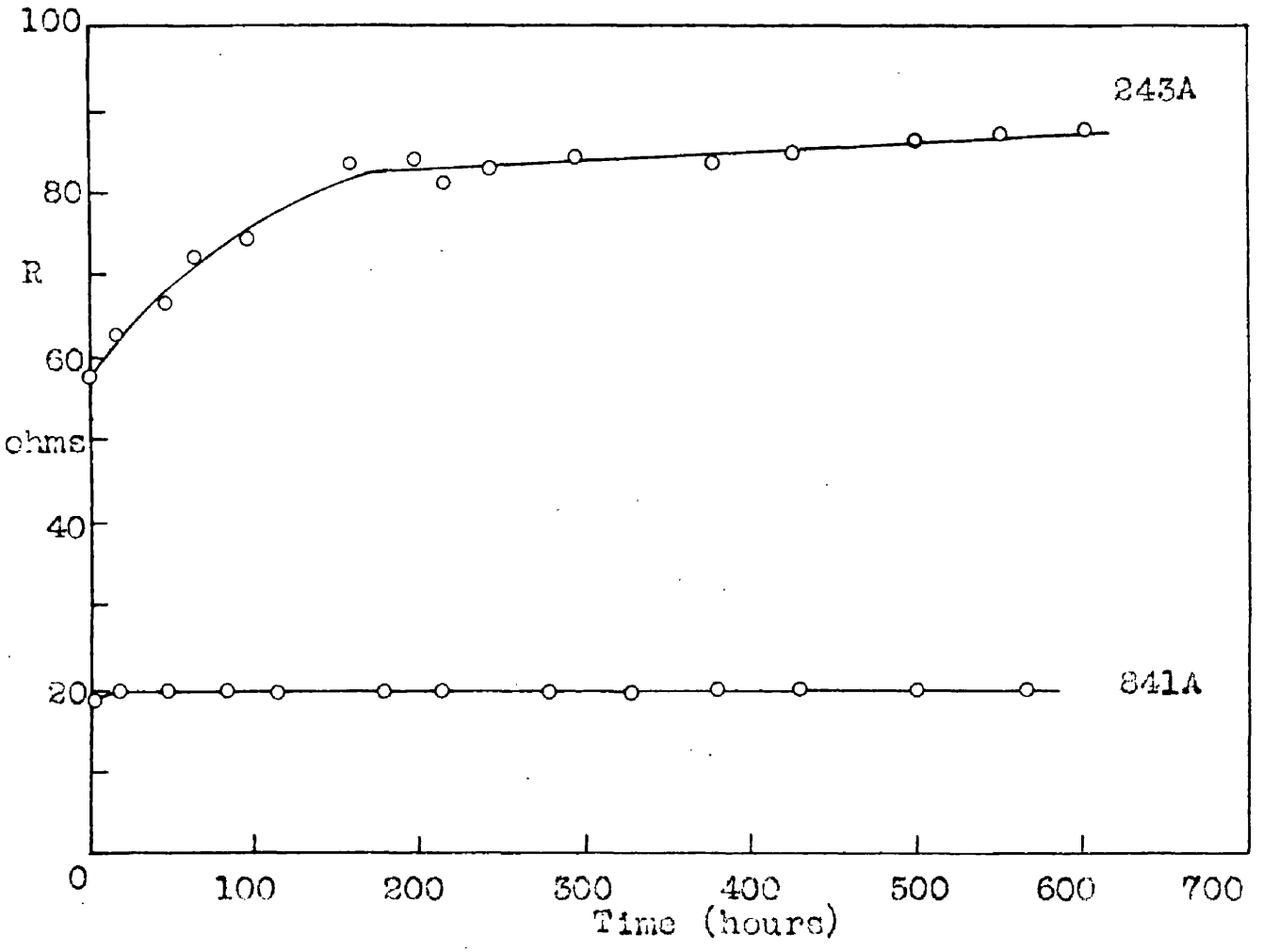


Figure 10.14. Variation of resistance (R) with time for ALUMINIUM films on glass.

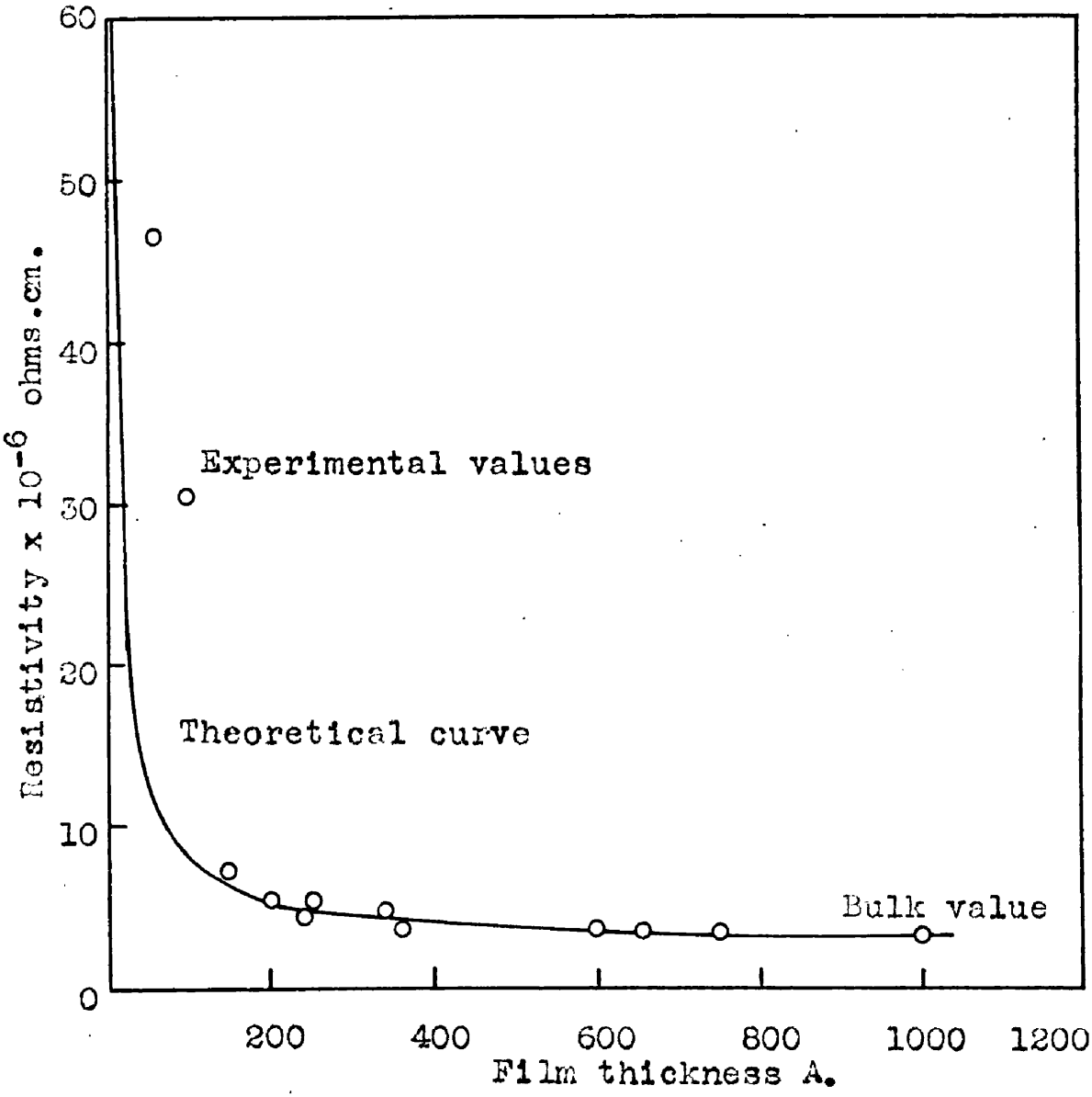


Figure 10.15. Resistivity versus film thickness for ALUMINIUM films.

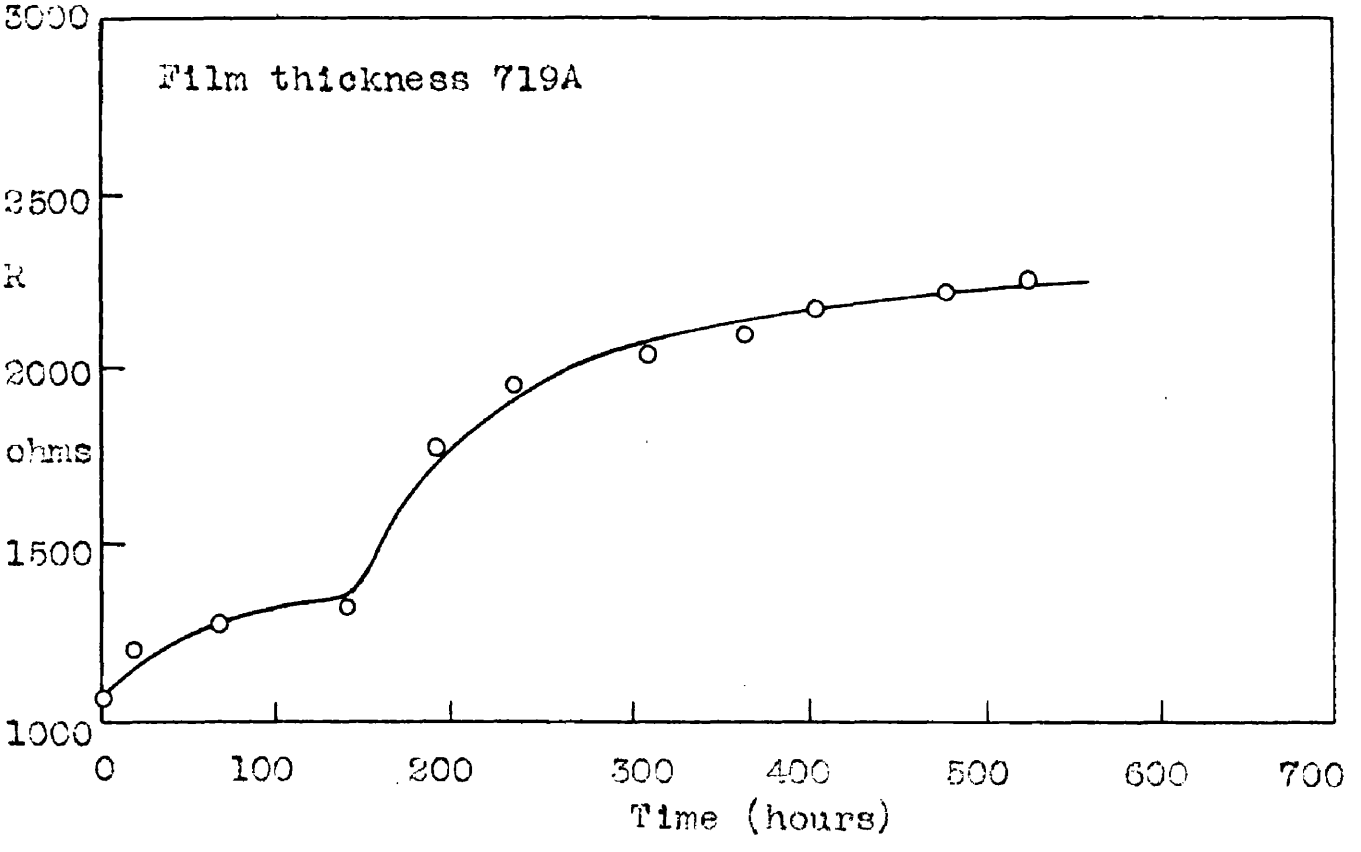


Figure 10.16. Variation of resistance (R) with time for MANGANESE films on glass.

4. Discussion

Group 1

It has been shown in the previous chapter that deposited films of the metals Au, Ag and Cu have a similar structure which appeared to be a collection of crystallites of random shape and size. On admitting air to the chamber after deposition of these films, gas could readily be adsorbed by this open film structure. Mostovetch and Vodar[59] have stated that this adsorbed gas could lower the potential barriers between crystals and cause a drop in resistance, and this is probably what occurred with Au, Cu and thick Ag films. It is possible that this effect also occurred with thin Ag films which would have an even more open structure than the thicker films and the time lapse before measurement may have prevented its detection. The increase in resistance observed with Au and thin Ag films was probably due to some recrystallisation and increasing aggregation due to favoured growth of larger crystals.

The type of open structure observed with films of these metals would account for the resistivities approaching values slightly higher than those of the bulk materials as the film thickness increased.

Group 2

All the films of the metals of this group showed an initial rise in resistance with time and, since all these metals are oxygen active, this was probably due to the formation of an oxide layer on the film surface. Cr and Ti both form a protective oxide coating which grows rapidly to its maximum thickness and, being continuous, prevents further oxidation. This would account for the resistance tending to a constant value after the initial rise. On the other hand, Ni and Fe do not form protective oxide coatings and the growth law indicates that the coating is permeable[62]. From the structure of these metals it would be expected that there would be diffusion of oxygen between the grains forming oxide inclusions. This would explain the continued rise of resistance observed for these metal films.

The initial resistivities of all the films examined in this group were higher than the bulk values though, in most cases, this was due, to some extent, to the thinness of the films. However, for Cr and Fe where thick films were examined, the resistivities were still found to be high and this could have been caused by the grain boundaries observed in the film structure. However, there is another possible reason. Hill and Weaver[63] have shown that the optical properties of Cr films can be explained by assuming

that thin chromium films are made up of very small ellipsoidal particles, each of these particles being surrounded by a very thin layer of oxide. It was suggested that, as the thickness of the films increased, the small particles become overlaid with successive layers of progressively larger oxide coated particles and at thicknesses greater than approximately 100A, the upper layers approximate to a continuous structure. This idea seems to be confirmed by the electron micrograph of a Cr film shown in the previous chapter. According to this concept, the resistivities of Cr films would decrease with thickness but would still tend in the limit to a higher value than that of the bulk material. However, the experimental curve shows a rise in the resistivity at a film thickness of approximately 400A. The rise cannot be explained by the concept of the structure described by Hill and Weaver. However, it could be due to the cracks observed in films of this metal. In a film of approximately 100A thick the width of these cracks was about 30A and their size and, therefore, their effect on the resistivity could increase with film thickness. Therefore, two factors could affect the resistivity of Cr films; firstly, the resistivity would be high due to the film structure but would decrease with increasing film thickness, and, secondly, the resistivity would increase with the increasing size and number of cracks

in the film. The combined effect of these two factors could give the resistivity versus thickness curve shown in Figure 10.9.

Group 3

The variation of resistance with time for films of the metals Zn, Pb, Sn and Cd was small. The difference in the variation of resistance with time for films of Zn and Cd can best be explained by reference to the film structures of these two metals. Zn films, comprising of large regular shaped crystals, showed an initial drop in resistance after which the resistance rose slightly. The initial drop could have been due to the slow adsorption of gas by the films which took place for some time after their deposition and lowered the potential barriers between the crystals. The ensuing rise in resistance could be explained by the continued growth of an oxide layer around each crystal. Electron diffraction has indicated the presence of oxide. The resistance of Cd films was found to be more stable than that of Zn films even though these films were shown to have a highly aggregated structure. However, the structure differs from that of Zn films in that, instead of being built up of large separate crystals, the films consisted of islands of atoms of irregular shape and size separated by wide channels

and gas could readily be adsorbed by this structure. As the thickness of these films increased, the aggregates would tend to joint up and the adsorption of gas would be slower. This would account for the observation of an initial drop in resistance in thick Cd films only, where the adsorption of gas would be relatively slow. The adsorption by thin Cd films may have been so rapid that the detection of the corresponding drop in resistance was prevented by the time lapse between deposition and the first resistance measurement. Again, the rise in resistance with time observed with thin Cd films was probably due to the formation of an oxide layer on the surface of the aggregates, the effect of which would be more apparent for thin films. It was shown in the previous chapter that the presence of oxide was observed in Cd films. The variation of resistance with time for films of Pb and Sn, being similar to that of Cd films, could indicate that their film structures were also similar to that of Cd films. Once again, electron diffraction indicated the presence of the oxide.

Group 4

The resistance measurements made on aluminium films appear to indicate that they have a continuous structure since the initial specific resistivities closely follow those predicted by Fuchs' theory. This theory assumes that the film is homogeneous and that the only hindrance to the passage

of the conduction electrons is due to the film boundaries. These resistance measurements appear to verify the evidence obtained by electron microscopy. The rise in resistance with time observed with these films would be due to the formation of an oxide layer on the film surface, the effect of which would be more apparent in the case of thin films.

The variation of resistance with time for Mn films showed two distinct stages. The initial rise in resistance would be due to the formation of an oxide layer on the film surface. However, the rise in resistance after 150 hours could be due to recrystallisation of the film. This was also suggested as the reason for the rupture of the formvar substrates in the previous chapter. It was also noted that the rise in resistance at 150 hours coincided with the rise in adhesion shown in Figure 7.9. As explained previously, recrystallisation would allow oxygen from the atmosphere to enter the film structure causing the increase in the adhesion.

5. Conclusions

The results of the measurements of the electrical properties of the metal films have substantiated further some of the suggestions made earlier as to the mechanism of adhesion and the part played by the film structure.

The initial drop in resistance was observed in a

number of films which had an aggregated structure and this could indicate that gas had been adsorbed into the structure. The adsorption of gas could explain the rapid rise in adhesion found with a number of copper films.

The initial specific resistivities of the films agreed with their structure inferred from electron microscopy. The high resistivities observed with iron and chromium films appeared to be due to either grain boundaries or oxide present in the structure. The presence of grain boundaries and oxide may also explain the high resistivities found with nickel, molybdenum and titanium films though the small film thicknesses of these films would account for part of the discrepancy.

Electron microscopy indicated that the structure of aluminium films was continuous, with an absence of grain boundaries and the resistivity measurements on these films compared so favourably with the theoretical values as to suggest that the films were homogeneous.

The variation of resistance with time for manganese films appeared to support the suggestion that recrystallisation of the film occurred after deposition and the rise in resistance corresponding to this recrystallisation coincided with the rise in adhesion.

CHAPTER 11

ADHESION OF METAL FILMS TO OTHER MATERIALS

1. Introduction

The adhesion of metal films to substrate materials other than soda glass has been examined. Films of a number of metals were deposited on fused silica, crystal faces and plastics, and their adhesion was measured by the adhesion measuring apparatus. The results of this investigation are described below.

2. Metal films on silica

Films of the metals Ag, Al, Cr, Fe and Cu were deposited by evaporation under the usual conditions on the optically polished surface of fused silica. This surface was cleaned in a similar manner to that of soda glass, that is, washed with 'Teepol', rinsed, dried and polished with lens cleaning tissue. The surface was finally cleaned by a glow discharge in vacuo.

The results of this examination are shown in Figure 11.1 where the adhesion of the films is given both as the vertical load in grams required to remove the film

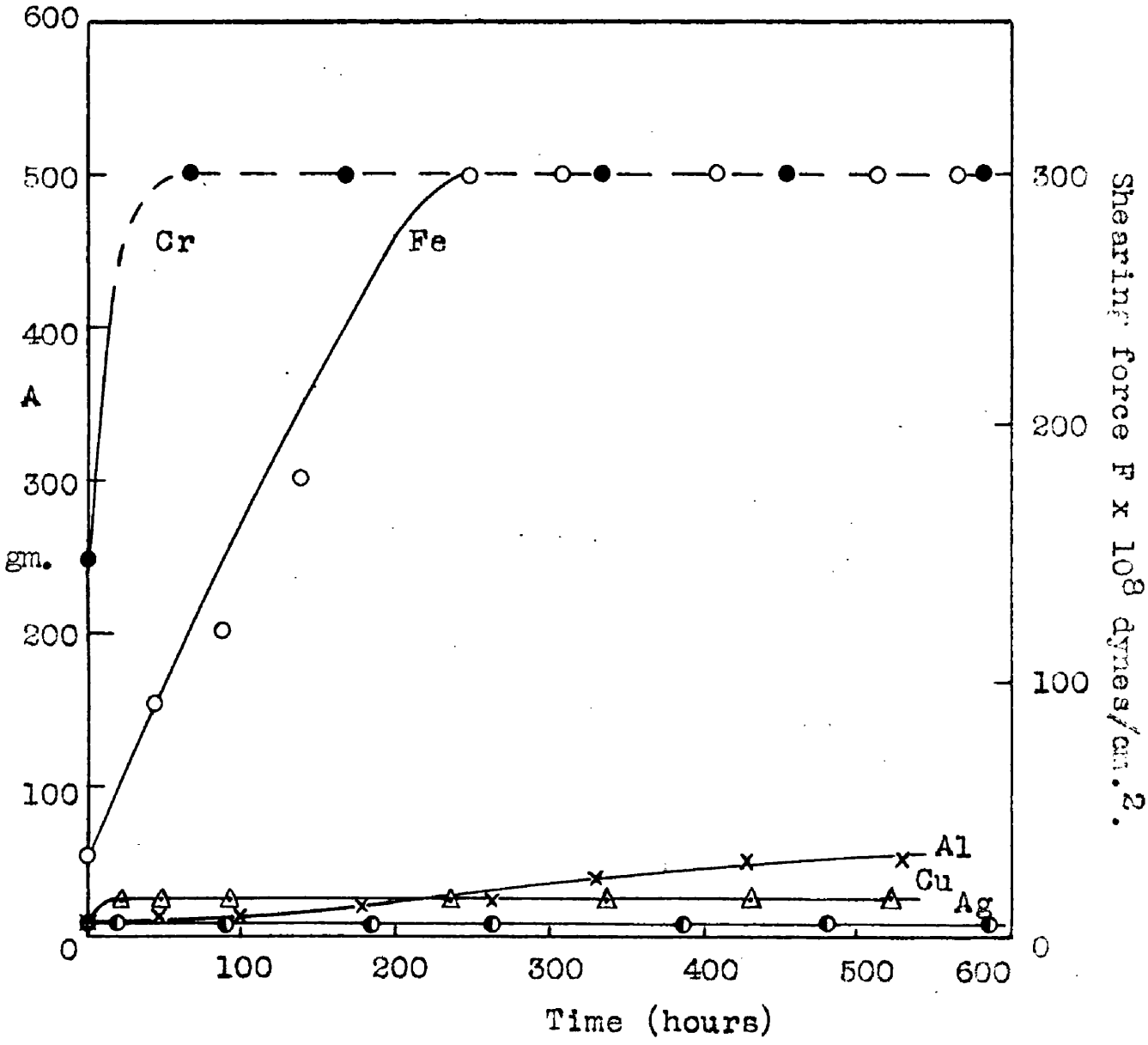


Figure 11.1. Variation of adhesion with time for metal films on silica.

and the corresponding shearing force in dynes/cm^2. It can be seen that there is a variation in adhesion with time and, in fact, the adhesion values and the way in which they vary are identical to the results obtained with metal films on soda glass.

It would appear that the adhesion of metal films to silica is due to a similar mechanism to that which causes the adhesion of the films to soda glass. That is, the adhesion of these metal films depends upon the affinity of the metal for oxygen and the structure of the film. The high adhesions observed are probably due to the formation of an intermediate oxide layer at the metal-glass interface. The absence of the large loosely bound alkali ions present in soda glass does not appear to affect the adhesion.

3. Metal films on crystal faces

Films of the metals Ag, Cu, Au, Al, Zn, Cd and Cr were deposited on freshly cleaved (100) faces of NaCl, KBr and KCl. These surfaces were only cleaned by a glow discharge in vacuo prior to the deposition of the films.

The adhesion of metal films on these crystal faces did not vary with time and the results are tabulated in Table 11.1. Columns 2 (a,b,c) and 3 (a,b,c) show the vertical load required to remove the films and the corresponding

TABLE 11.1

THE ADHESION OF METAL FILMS TO THE (100) FACES OF VARIOUS CRYSTALS

Metal	Adhesion gm.			Shearing Force F 10^8 dynes/cm^2			van der Waals' Adhesive Energy E K.cal./mole		
	NaCl	KBr	KCl	NaCl	KBr	KCl	NaCl	KBr	KCl
Ag	10	9	10	8.1	5.0	5.0	2.7	2.5	2.1
Cu	12.5	-	14	9.0	-	6.0	3.4	-	2.9
Au	7	7	6	6.7	4.7	4.0	2.0	1.9	1.4
Al	10	16	14	8.1	4.3	6.0	3.8	3.5	2.9
Zn	5	-	-	5.7	-	-	2.3	-	-
Cd	3.5	-	-	4.8	-	-	1.9	-	-
Cr	2.5	3.5	4	4.0	3.5	3.5	1.6	1.4	1.3

shearing force respectively. The van der Waals' adhesive energy between the films and the surfaces, calculated as described in Chapter 2, are shown in Column 4 (a,b,c).

The relationship between the shearing force, F, and the energy, E, binding a metal film to a substrate surface was given in Chapter 6 as

$$E = \tfrac{1}{2}Fxx_2x_3$$

where x is the distance between two adjacent equilibrium positions in the substrate surface and x_2 and x_3 are the lattice dimensions in the metal film. Taking the values for a copper film on the (100) face of NaCl as an example, E is 3.4 K.cal./mole, x is 2.82Å, and both x_2 and x_3 are 2.55Å. Substituting these values in the above equation, the value for the shearing force, F, is found to be 1.7×10^{10} dynes/cm^2. From Table 11.1 it can be seen that the experimental value for F is 9.0×10^8 dynes/cm^2 which is an order of magnitude lower. However, this discrepancy is to be expected since the equation

$$E = \tfrac{1}{2}Fxx_2x_3$$

gives the maximum value of F.

The values of x, x_2 and x_3 are very similar for each metal-substrate pair examined and therefore the above

equation could be written as

$$E \simeq \text{constant} \cdot F$$

Figure 11.2 shows the experimental values of F plotted against the van der Waals' adhesive energy and it can be seen that there is a linear relationship between F and E.

It would appear that the adhesion of metal films to crystal faces is due to van der Waals' forces alone and there is no evidence of a chemical reaction between the metal films and the crystal surfaces.

4. Metal films on plastics

The plastics selected for this examination were Perspex, Polystyrene, C.R. 39 (columbia resin), and Xylonite (celluloid). Sheets of these materials were examined closely and substrates of suitable shape and size were cut from areas relatively unmarred by scratches and other defects. These substrates were then cleaned, in the same manner as glass, and subjected to a glow discharge in vacuo. Apart from cleaning the surface this glow discharge did not seem to affect the plastics since there was no sign of discoloration or warping due to overheating.

The results of the adhesion measurements on metal films deposited on the above substrates are shown in Table 11.2. No variation in adhesion with time was observed

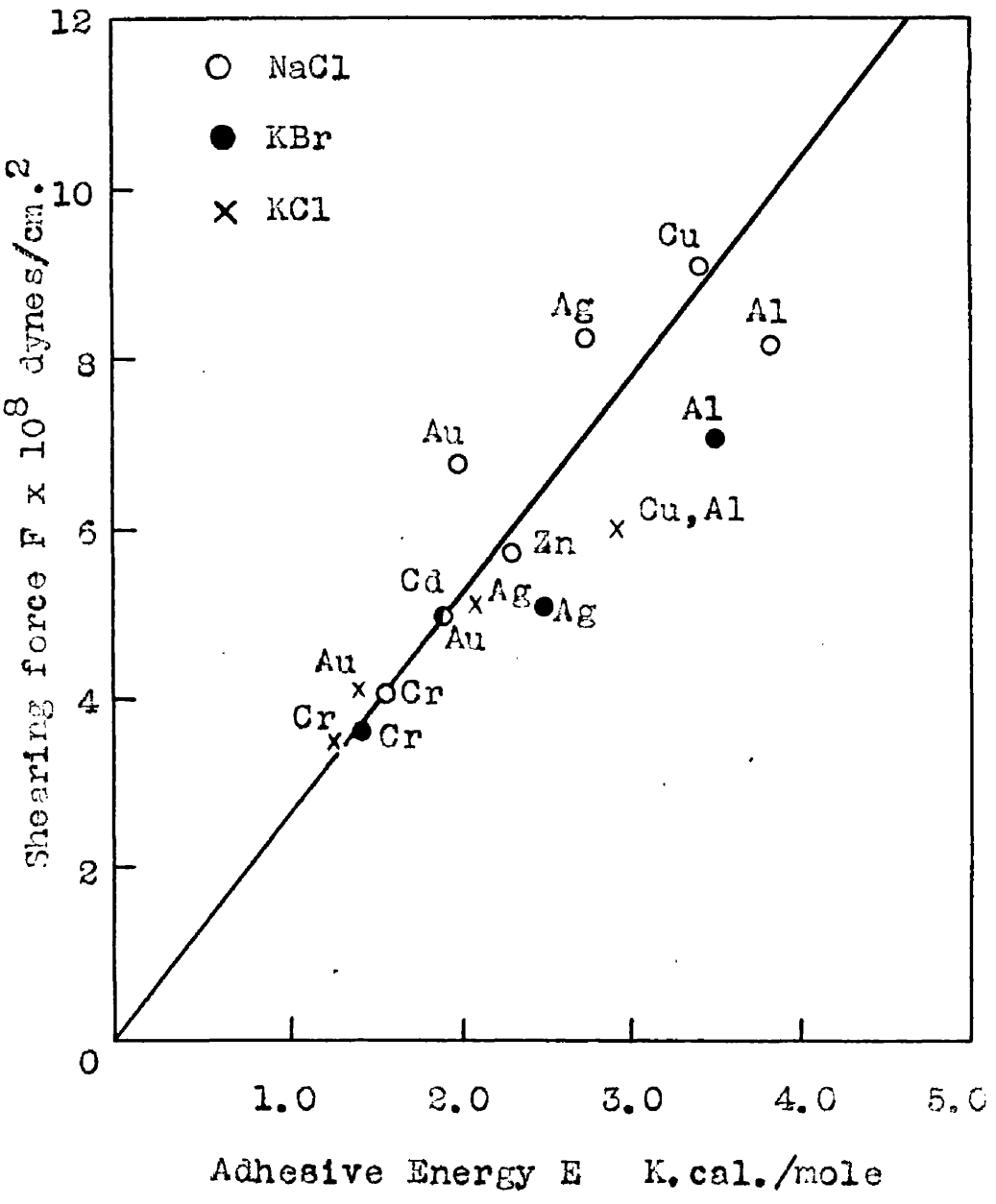


Figure 11.2. Shearing force required to remove metal films from the (100) faces of a number of crystals against the van der Waals' adhesive energy.

TABLE 11.2

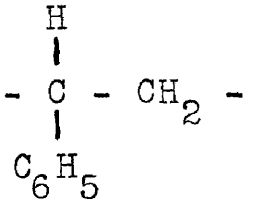
THE ADHESION OF METAL FILMS TO PLASTIC MATERIALS

Metal	Shearing Force F x 10^8 dynes/cm.^{2}			
	Polystyrene	Perspex	Xylonite	C.R.39
Ag	13.2	30.0	15.3	24.6
Cu	10.3	15.0	-	-
Al	7.0	11.6	6.3	8.1
Zn	10.3	11.6	-	-
Cr	4.2	5.2	4.0	4.4

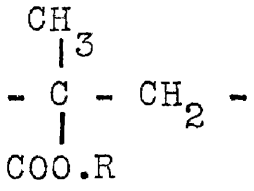
with these films. It was found that silver had a very strong adhesion to all the plastic surfaces, in fact, silver films were non-removable from C.R. 39 and Xylonite, the values of F being in effect the strength of the substrates. On the other hand, chromium films could be removed easily from the surface of the plastics. This result is a direct contradiction of the statement by Holland[64] that 'oxygen active metals tend to have the greatest adhesion to plastics'.

The very high adhesion of silver cannot be explained in terms of van der Waals' forces and is probably due to a chemical reaction between the film and the plastic surface. Silver is known to react with organic substances, for example, there is a reaction between acetylene (C_2H_2) and silver giving silver acetylide (C_2Ag_2). However, one can only tentatively suggest the possible reaction between a silver film and the plastic surfaces, the simplest fundamental units of which are shown in Figures 11.3 and 11.4. Polystyrene has the simplest structure and it might be possible for a silver atom to replace the hydrogen atom in the plastic surface especially since this hydrogen atom could be in a reactive state due to the presence of the benzene ring. In the case of Perspex, silver could react with the $COOCH_3$ group and displace the CH_3 radical. The most likely sites for reaction between silver and the surface of Xylonite are probably at R, R' or R'', since

Polystyrene



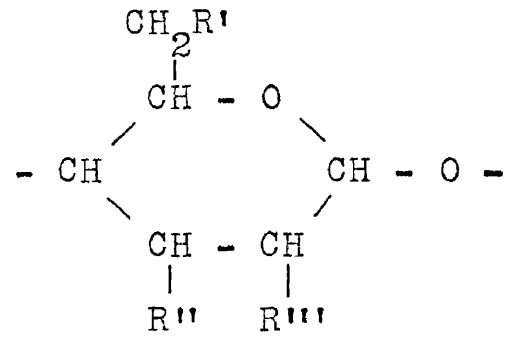
Perspex (methyl methacrylate) - polyester



R is an alkyl or aryl radical such as CH_3.

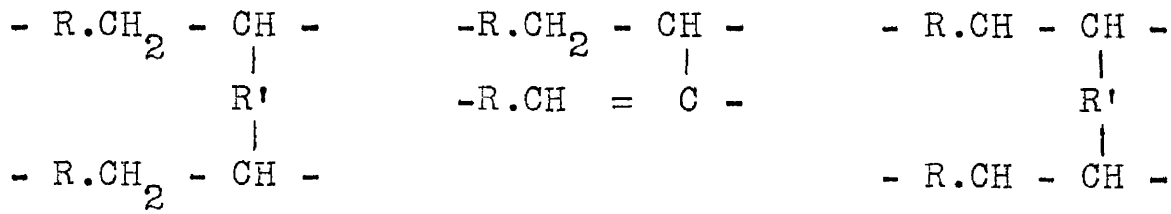
Figure 11.3. The simplest fundamental units in plastic materials.

Xylonite (celluloid)



R', R'' and R''' represent OH groups in cellulose which are partially or fully replaced by - $O.NO_2$ groups.

C.R. 39 (columbia resin) - polyester resin



(1) (2) (3)

$RCH_2(CH\cdot)$, $RCH{:}(C\cdot)$, or $R(CH\cdot)(CH\cdot)$ represent part of a linear or branched chain and R' is a complex divalent group.

Figure 11.4. The simplest fundamental units in plastic materials.

these represent OH groups in cellulose which are partially or fully replaced by - $O.NO_2$ groups to give the nitro-cellulose structure. C.R. 39 is a polyester resin and can have three possible fundamental units and it is difficult to say with which part of the structure the silver would react.

Though the adhesion of Cu, Zn and Al films was not so high as that of Ag, their adhesion was still somewhat greater than that of chromium. However, Cu, Zn and Al films could also have reacted to some extent with the plastic surfaces since these metals can form organo-metallic compounds. It is very unlikely that chromium would react with the plastic surfaces and the chromium films were probably bound to the surfaces by van der Waals' forces. This would account for the poor adhesion observed with these films. The shearing force required to remove chromium films from plastic surfaces was the same as that required to remove from crystal faces the films which have been shown to be bound by van der Waals' forces.

Though the actual mechanism of the adhesion of metal films on plastic surfaces is rather vague, it is fairly certain that there is, in a number of cases, a chemical reaction between the metal films and the plastic surfaces. The most

reactive of these metals appears to be silver. On the other hand, chromium films are apparently bound to the surfaces by van der Waals' forces alone.

CHAPTER 12

GENERAL CONCLUSIONS

It was shown in Chapter 1 that there was no suitable method of measuring the absolute value of the adhesion between a thin film and the surface upon which it was deposited, particularly if the films were of the order of 100 - 2000A thick and there was strong adhesion between the two media. However, there were a number of methods available for a comparative measure of adhesion of which the only suitable one appeared to be that described by Heavens[21]. In this method a loaded steel point of smooth contour was drawn across the film surface and the load required to remove the film completely from the surface was taken as a relative measure of the adhesion. Heavens gave no analysis of this method and there was some doubt as to what was actually measured by the load on the point. Therefore, before this method was used in the present investigation, a complete study of the method was made. It was shown experimentally that the load required to remove the film from a surface was related to the nature of the interface between the two media but was independent of other factors such as film thickness, the hardness of

the film material and the formation of a protective coating on the film surface. The mechanism of the method of measuring adhesion was also examined theoretically and it was found that an absolute value of the adhesion, or the shearing force required to remove the film, could be calculated from the load on the point, the radius of the point, and the indentation hardness of the substrate material.

This method gave reproducible results and proved to be very satisfactory. A comparative measure of the adhesion could be obtained for films on the same substrate by simply comparing the loads required to remove the films. On the other hand, the adhesion of films on different substrates could be compared by use of the calibration curves calculated for the apparatus. Furthermore, a wide range of adhesions could be measured and the measurement of high adhesions was only limited by the strength of the substrate material.

Using the method described by Rhodin[6], the experimental values for the heat of condensation obtained in Chapter 2 for the metals silver, aluminium, and cadmium on soda glass appeared to indicate that the impinging metal atoms were, in these cases, initially bound to the surface by van der Waals' forces. This was in agreement with the poor initial adhesion observed with these films, the shearing

force required to remove the films being approximately 10×10^8 dynes/cm^2. However, films of many metals showed a much greater adhesion and cracking of the glass substrate occurred before the films could be removed. This happened at loads of the order of 500 grams indicating that the shearing forces required to remove the films were greater than 300×10^8 dynes/cm^2. Adhesions of this order cannot be explained in terms of van der "aals' forces. Furthermore, even where the initial adhesion was poor, there was often an increase in adhesion with time which, together with the wide range of adhesion values, would suggest that chemical bonds were formed at the metal-glass interface.

"eyl[12] has suggested in many cases that the adhesion of metal films to glass could be strong if there was a continuation of the glass structure which could be in the form of an intermediate oxide layer. Bateson[14] proposed that the oxide might be formed by the reaction of the impinging metal atoms with the OH groups present on the glass surface. The adhesion results shown in Chapter 7 do indicate that, in general, the oxygen active metals have a high adhesion to glass. However, the oxygen present in these OH groups on the surface is limited and it is doubtful whether a complete oxide bond would be formed between the metal atoms and the glass surface and this reaction would certainly not account for the thick intermediate oxide layers

observed by Stahl[17]. The films in the present investigation were deposited at fairly fast rates at a pressure of approximately 10^{-5} mm. Hg in a residual atmosphere of air and under these conditions the ratio of oxygen molecules to metal atoms striking a square centimeter of the substrate surface per second was of the order of 10 to 1. It was suggested that these impinging oxygen molecules would assist in the formation of a complete oxide bond between the metal film and the glass surface and the growth of an intermediate oxide layer at the interface. The adhesion results on films deposited in various atmospheres and at various pressures described in Chapter 8 were in accordance with this suggestion. It was found that films of oxygen active metals deposited in an oxygen free atmosphere had a very poor adhesion to glass. However, when the films were deposited in an excessive atmosphere of oxygen even the initial adhesion was high and the films could not be removed from the surface immediately after deposition. Therefore, it appeared that the intermediate oxide layer was formed during deposition of the films.

It was shown in Chapter 7 that a number of metal films exhibited ageing effects. The adhesion of the films was initially poor but increased with time and, in some cases, became non-removable from the glass surface. The way in which the adhesion increased appeared to indicate

that a diffusion process was taking place, the process being one which promoted the growth of the intermediate oxide layer so that the film had its maximum adhesion when the growth of the layer was complete. The growth of the layer would, of course, be dependent upon oxygen reaching the metal-glass interface and this oxygen could come from gas trapped within the film structure during deposition or from the atmosphere after deposition. The diffusion of the gas to the interface would be dependent upon the structure of the film since its permeability would control the amount and rate of gas reaching the interface. Examination of the film structure by electron microscopy, supported by the results of electrical measurements on the films, has shown that the adhesion of metal films does depend to a large extent upon the film structure.

Electron microscopy showed that films of gold, silver and copper had an open aggregated structure and the electrical measurements on these films appeared to support the suggestion of Mostovetch and Vodar[59] that gas was adsorbed by this type of structure after deposition. The adhesion of gold films was not affected by this adsorption since there would not be any reaction at the metal-glass interface between the metal and the oxygen present in the adsorbed gas though the slight increase in adhesion with

time observed for silver films could indicate that a weak oxide bond was formed with the glass surface. However, the shearing force of 10 x 10^8 dynes/cm^2 required to remove these films suggested that they were bound to the surface by van der Waals' forces. On the other hand, copper forms a fairly strong oxide and a reaction between the metal and the oxygen present in the adsorbed gas would account for the rapid rise in adhesion with time to a value of 60 x 10^8 dynes/cm^2 which was much greater than that for silver and gold.

The slower increase in adhesion with time observed, for example, with iron and nickel films appeared to be due to their continuous film structure, the diffusion of gas, either trapped within the structure or from the atmosphere, being along the grain boundaries observed in these films. Iron films deposited in a residual gas of hydrogen had a low initial adhesion but there was a steady increase with time. Since there would be very little oxygen in the gas trapped within the structure during deposition, the increase in adhesion would seem to be caused by diffusion of gas from the atmosphere along the grain boundaries. On the other hand, aluminium and chromium films deposited in a residual gas of hydrogen and argon respectively had a poor adhesion which did not

increase with time. Again very little oxygen would be trapped within the film structure during deposition and since both these metals would form protective coatings on their surfaces it is doubtful whether any gas from the atmosphere would be able to enter the film structure after deposition. Thus no oxide layer would be formed at the metal-glass interface and this would account for the poor adhesion. However, aluminium and chromium films deposited at 10^{-5} mm. Hg with a residual gas of air showed an increase in adhesion with time; in the case of chromium the films soon became non-removable. The rate of film formation for chromium was slow and this would allow a high initial adhesion and a large amount of gas to be trapped within the structure. Even if the formation of a protective coating on the film surface prevented gas from the atmosphere entering the structure, there would probably be enough gas containing oxygen trapped within the structure to complete the formation of the intermediate oxide layer. Rapid diffusion of this gas to the metal-glass interface could again be along grain boundaries. On the other hand, aluminium films were formed rapidly preventing the formation of an oxide bond to the glass surface and allowing only a very little gas to be trapped within the structure. This would account for the poor initial adhesion and, since

no gas from the atmosphere would penetrate the protective coating, the growth of the intermediate oxide layer would be limited and the corresponding increase in adhesion with time would be small. The electrical measurements on chromium films appear to indicate the presence of oxide within the film structure whereas those on aluminium films indicate a homogeneous structure devoid of defects. Finally, when aluminium and chromium films were deposited at high pressures the films were found to be non-removable immediately after deposition which seemed to indicate that the oxide layer at the metal-glass interface had been formed during deposition of the films.

For oxygen-active metals, it would appear that, in general, good adhesion of the metal films to glass is possible when there is sufficient oxygen present to enable the formation of the intermediate oxide layer at the metal-glass interface during deposition of the film. In some cases this may mean depositing the metal at a pressure of 10^{-3} to 10^{-4} mm. Hg with a residual gas containing oxygen. However, at these pressures not only are there a large number of oxygen molecules bombarding the substrate but the mean free path of the metal atoms is small. This may have the opposite effect on the adhesion in that the metal atoms will make a large number of collisions with

the residual gas molecules on their way to the substrate and may, in fact, be prevented from reaching the substrate. The optimum condition would appear to be when not only is there sufficient oxygen present to enable the formation of an intermediate oxide layer but when the stream of metal atoms is not impeded to any great extent by the residual gas.

The low melting point metals have a poor adhesion to a glass surface even though their affinity for oxygen is quite strong. The film structure again played an important role but, in this case, in a different way. Films of these metals do not build up in the usual manner but, according to McLauchlin, Sennett and Scott[57,58], the impinging metal atoms condense instantaneously on the glass surface in the form of large crystals or aggregates. Electron microscopy showed these crystals and aggregates to be separate from one another and, since only a small area of the film at the interface would be in actual contact with the glass surface, the adhesion would therefore be poor.

The difference between the surfaces of soda glass and fused silica is that the surface of soda glass contains large loosely bound alkali ions. However, these ions do not appear to affect the adhesion since the adhesion of metal films deposited on both surfaces was shown to be identical. It seems that the mechanism of adhesion in both cases was the same.

The heats of condensation of metal films on crystal faces indicated that these films were bound to the surfaces by van der Waals' forces. This was further supported by the poor adhesion of the films to the surfaces, the shearing force required to remove the films being 3×10^8 to 10×10^8 dynes/cm.^{2}, that is, the same order of magnitude as the force required to remove a gold film from a glass surface. The adhesion of the metal films to the crystal faces did not vary with time and there was no evidence of any chemical reaction occurring between the metals and the crystal surfaces. A chemical reaction or chemisorption would be inferred from the high value for the heat of condensation obtained for aluminium on the (100) face of NaCl by Rhodin[6] but is not supported by the above results.

There does appear to be a chemical reaction between a number of metal films and the surfaces of plastics. Silver films were found to be almost non-removable and there was also strong adhesion between the surfaces and films of copper, zinc and aluminium. Owing to the complex nature of the plastic surfaces, it is only possible to make tentative suggestions as to the reactions which take place between the metals and the plastic surfaces. On the other hand, chromium films had a very poor adhesion to plastic

surfaces and the shearing force required to remove these films appeared to indicate that the films were bound to the surfaces by van der Waals' forces.

The films in this investigation were deposited under conditions similar to those used in commercial and laboratory practice and no elaborate precautions were taken. Therefore, the results of this investigation could be applied to that type of procedure.

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MEASUREMENT OF THE THICKNESS OF THIN FILMS BY MULTIPLE-BEAM INTERFERENCE

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THE multiple-beam interference method for the measurement of the thickness of thin metallic films developed by Tolansky[1] is now a well-established technique. The film, the thickness of which is to be measured, is deposited on a substrate, part of which is covered to give a sharp edge to the film. An opaque metallic reflecting layer is then deposited over the edge of the film. The step in this overlayer is measured by using it as one surface of an interferometer and viewing the multiple-beam fringe system in reflexion. Provided that the overlayer assumes the exact contour of the surface, this step-height will give the thickness of the film underneath.

Tolansky has given adequate evidence that silver fulfils the necessary requirements both in its high reflectivity and its ability to contour the surface. Some workers have tried metals other than silver, using fringes of equal thickness[2,3] and fringes of equal chromatic order[4]. In both fringe systems the displacement of the fringes at the discontinuity caused by the step-edge gives the height of the step in the opaque layer. However, Avery[2] has shown that the thickness of a silver film as measured by multiple-beam interference may vary considerably with the metal used for the overlayer. It was found that the value for the thickness of a silver film was 25 per cent greater when measured using a chromium overlayer than the thickness when measured with a silver overlayer. Avery explained this discrepancy by considering the silver film to have an aggregated structure[5]. He suggested that atoms of silver would enter the interstices of a silver film more easily than atoms of chromium, and that this would lead to a 'packing-in' effect for silver on silver but not for chromium on silver. Another explanation for this discrepancy was put forward by Scott, McLauchlin and Sennett[4]. They suggested that the structure of the chromium overlayer adjacent to the substrate might be less aggregated than that of the silver film;

but no further experiments were carried out to check the results of Avery.

The occurrence of this discrepancy was not confirmed by Heavens[3]. No evidence of 'packing-in' of the atoms of the overlayer material into the interstices of the film was observed. This disagreement may be due to the experimental conditions employed by each worker, and the lack of these details in the work of Avery makes comparison of the results very difficult.

Experiments have been carried out in this Department on the measurement of the thickness of thin silver films, using both silver and chromium as the overlayer material. A standard experimental procedure was adopted for the deposition of these films, which were evaporated on to selected glass microscope slides. Fig. 1 shows the position on the substrate of the silver film (W), and the overlayer films of silver (X) and chromium (Y). These three films were deposited in succession without admission of air between evaporations. A mechanical device was used to arrange the slide normally above each source in turn, at a distance of 30 cm. Assuming a point source, the maximum possible variation in thickness over the whole surface would not exceed 1 per cent. Since the silver film is symmetrically placed with respect to the silver source, the thicknesses at the two ends should be identical, and this was confirmed within experimental error. The slide was cleaned with 'Teepol', hydrogen peroxide (20 vol.), dried with cotton wool, and polished with lens-cleaning tissue. The surface was finally cleaned electrically *in vacuo*. The films were deposited at a pressure of 10^{-4}–10^{-5} mm. mercury. In view of its marked effect on the structure of thin metallic films[6], the rate of evaporation was considered an important experimental condition. Silver films were deposited at evaporation-rates between 1 and 60 A./sec. approximately. In each case the rates of evaporation of the silver and chromium overlayer films were kept constant at approximately 20 A./sec. and 3 A./sec.,

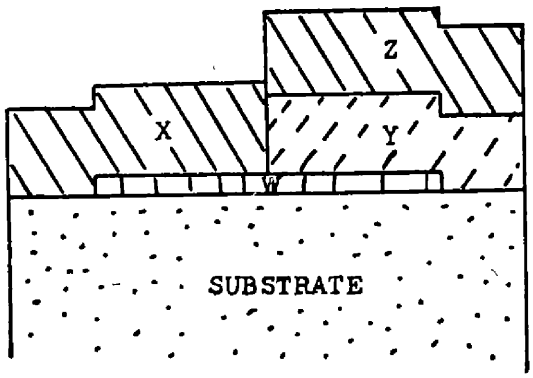

Fig. 1

Table 1

Thickness by X (A.)	Thickness by Y (A.)	Thickness by Z (A.)	Discrepancy $\frac{Y-X}{X}\times 100$	Discrepancy $\frac{Z-X}{X}\times 100$	Rate of evaporation (A./sec.)
337	395	326	17	3	28
461	562	454	22	2	22
203	215	216	6	6	11
245	262	240	7	2	3
456	466	427	2	6	35
577	620	613	7	6	16
939	924	958	2	2	57

respectively. The thicknesses of the silver films were measured by multiple-beam interference fringes of equal thickness viewed in reflexion.

The results of these investigations are shown in Table 1. They indicate that when the chromium overlayer is opaque, then there is no discrepancy in the thickness of the silver film as measured by the two different overlayers. However, when the chromium overlayer is not opaque, then a discrepancy of the type found by Avery occurs. The variation of the rate of evaporation of the silver film appears to have no effect on the results. The first two tests in Table 1 are with a non-opaque chromium overlayer, whereas the remaining tests are with opaque overlayers. The discrepancy in the thickness of the silver film as measured by X and Y is expressed as a percentage of X.

Schulz and Scheibner[7] have shown that when a beam of light strikes a metal film at normal incidence, the phase change at reflexion can be related to the thickness of the film. This phase change becomes constant at a certain film thickness, in the case of silver at 500 A. It can be assumed that there is a similar thickness for chromium, and for films below this critical thickness the phase change will be affected by the underlying film or substrate. The discrepancy in the thickness measurements when a non-opaque chromium layer is used may then be caused by a difference in the phase change at reflexion on the two sides of the step-edge since the underlying substances are different. That is, the fringe displacement at the step-edge would consist of the displacement due to the thickness of the silver film plus a displacement due to a difference in phase change.

This proved to be the case. An opaque silver layer (Z in Fig. 1) was deposited on the chromium overlayer; when the step in this layer was measured, a thickness for the silver film (W) was obtained which agreed with that as measured by the silver overlayer (X), as shown by the first two sets of results. It is

concluded that the disappearance of the discrepancy after this final evaporation is due to the elimination of the difference in phase change. This conclusion is supported by the results of tests with an opaque chromium overlayer. There is then no change in the measured thickness value when the silver layer (Z) is deposited on the chromium. The measured height of the step in this layer is in good agreement with the values given by the silver and chromium overlayers X and Y.

The investigation is being continued to determine the critical thickness of chromium and the variation of phase change at reflexion with thickness.

One of us (P. B.) wishes to thank Metropolitan Vickers Electrical Co., Ltd., for the provision of a postgraduate scholarship to undertake this work.

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ERRORS IN THE MEASUREMENT OF THE THICKNESS OF THIN FILMS BY MULTIPLE-BEAM INTERFEROMETRY

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The Tolansky[1] method for the measurement of the thickness of thin films by multiple-beam interference techniques is now well established. Briefly, the film, the thickness of which is to be measured, is deposited on a flat smooth substrate. The film should have a sharp edge so that a step is formed when the film and the adjacent substrate are coated with an opaque highly reflecting metallic layer. The height of this step is measured by using the highly reflecting layer as one surface of an interferometer and viewing the multiple-beam fringe system by reflection. Provided that the overlayer assumes the exact contour of the surface, this step-height will give the thickness of the film underneath.

There are two ways in which a sharp edge can be given to an evaporated film. Part of the substrate can be

shielded during the deposition of the film, the shield being removed for the deposition of the overlayer. Alternatively, Scott, McLauchlan and Sennett[2] have suggested that a sharp-edged step could be formed by gently drawing a not-too-sharp needle across the film prior to the deposition of the overlayer so that the film is removed, leaving a clear channel. However, they point out that care must be taken not to mar the substrate, in their case glass, marring being detected by the shape of the fringes.

In the course of investigating the adhesion of thin films to glass[3], it was found that serious errors could be made in the measurement of the thickness of the films when the method described by Scott, McLauchlan and Sennett was used. A number of metals were investigated and in each case a film of the metal was deposited by evaporation on to a glass surface, a sharp edge being given to each film by covering part of the substrate during deposition. A number of channels were also made in each film by drawing a loaded steel point of smooth contour across the film surface. The point used in this investigation had a tip radius of 0.003 cm. and the load on the point was varied from 0 - 500 grams, the glass substrate tending to crack at this upper limit. The film and the substrate were then coated with an opaque silver layer and the film thickness and the depths of the channels or scratches were measured by viewing

the multiple-beam interference fringes of equal thickness by reflection. The results of one such set of measurements are shown in Fig. 1. In this case, the thickness of a chromium film was found to be 302A but the depth of the scratches made at loads greater than about 5 grams were always greater than this value and increased with the load on the point. It has been shown[4] that plastic deformation of the glass substrate occurs when a load exceeding 2 grams is applied to a point of tip radius 0.003 cm. pressing on it. It was found that the load required on the point to give a clear channel depended upon the adhesion of the metal film to the glass substrate and, for nearly all the films examined, a load greater than 2 grams was required to give a clear channel. Therefore, deformation of the substrate would occur. Variation of the tip radius of the point would not eliminate the deformation of the substrate since it has been shown[4] that when the radius is decreased plastic deformation occurs at even lighter loads, whereas, when the radius is increased, a greater load is required to give a clear channel.

Scott, McLauchlan and Sennett measured the thickness of films of Ag, Au, Cu, Al, Sb and Cr. Table 1 shows the load on a point of radius 0.003 cm. required to give a clear channel in films of these metals together with the deformation of the substrate. It can be seen that if the depth of the channel

was taken as the film thickness then very serious errors could occur, especially if the film adheres strongly to the substrate and a large load is required to give a clear channel. Scott, McLauchlan and Sennett have stated that a check was made between the film thickness and the depth of the channels and good agreement was found. However, it is possible that this check was made on a poorly adherent film such as silver where the discrepancy would be within the experimental error and this would account for the agreement.

It can be seen that even when a light pressure is applied to a point to give a channel by which the thickness of a film may be measured serious errors occur. These errors are even greater when excessive pressure has to be applied to the point to obtain a clear channel in a film which adheres strongly to the substrate. It would appear that this method of forming a sharp edge to the film is unsatisfactory and any measurements made using this technique should be treated with caution.

One of us (P.B.) wishes to thank Metropolitan Vickers Electrical Co., Ltd., for the provision of a postgraduate scholarship to undertake this work.

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TABLE 1

Metal	Load for clear channel gm.	Deformation of substrate A.
Ag	7	23
Au	2	0
Cu	30	160
Aℓ	5	18
Sb	-	-
Cr	100	273

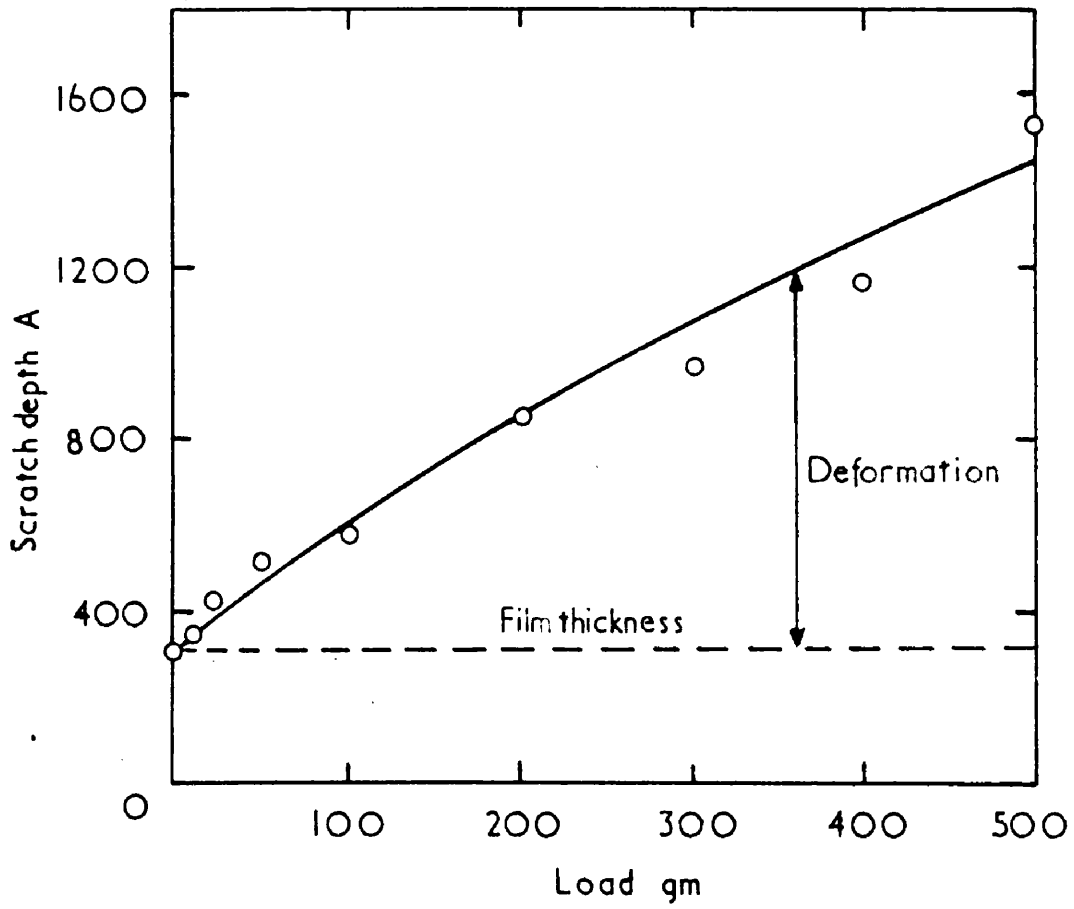
1600
1200
800
400
0
Scratch depth A
100
200
300
400
500
Load gm
Deformation
Film thickness

Fig. 1

THE ADHESION OF THIN METALLIC FILMS

by

P. Benjamin, A.R.C.S.T.

SUMMARY

A Thesis

Submitted for the Degree of Doctor of Philosophy

in the Faculty of Science

University of Glasgow

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SUMMARY

Methods of measuring adhesion of thin films have been considered and an analysis has been presented of a method due to Heavens. In this method a loaded steel point of smooth contour was drawn across the surface of the film, and the load required to remove the film completely from the surface was taken as a relative measure of the adhesion. There has been some doubt as to what is actually measured by the load on the steel point. However, it has been shown experimentally that the load required to remove the film from the surface does depend upon the adhesion between the film and the supporting medium. The mechanism of the method has been examined theoretically and it has been found that an absolute value of adhesion can be calculated from the load on the point, the radius of the point, and the indentation hardness of the surface material. Using this method of measuring adhesion, the adhesion of thin metallic films deposited by vacuum techniques on to the surface of various materials has been investigated.

The adhesion of metal films to the surface of glas has been thoroughly examined and it has been found that there are a number of factors involved in obtaining the

maximum adhesion. It appears that the metal atoms impinging on the glass surface can either be bound to the surface by van der Waals' forces or react chemically with the surface to form an oxide bond. The nature and pressure of the residual gas during deposition of the films and the rate of film formation determine the extent of this reaction at the metal-glass interface. However, the reaction between the metal and the glass surface can continue for some time after deposition as the measurement of adhesion over a period of time has shown and the rate and extent of the reaction depends upon the structure of the films. It would appear that a metal film has its maximum adhesion to a glass surface when a complete intermediate oxide layer has been formed at the metal-glass interface. In some cases when this occurred the films could not be removed from the glass surface. This is confirmed by the behaviour of metal films deposited in various atmospheres and at different pressures. The structure and electrical properties of the films are in general agreement with the theory.

The adhesion of metal films to crystal faces appears to be due to van der Waals' forces alone, but these forces cannot explain the adhesion of metal films deposited on the surface of plastics where a chemical reaction seems to occur in some cases. However, the complicated nature of the